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# P. Alois Gatterer S. J. †.

*Alois Gatterer* wurde am 18. Januar 1886 in Reichraming, Oberösterreich, als Sohn eines Forstverwalters geboren, absolvierte das Gymnasium im Petrinum, Linz, und trat 1905 in den Jesuitenorden

ein. Nach Abschluß seiner theologischen Ausbildung 1915 zum Priester geweiht, studierte er Chemie und Physik an der Universität Innsbruck, wo er 1922 mit Auszeichnung promovierte. 1924 habilitierte er sich an der theologischen Fakultät für die naturwissenschaftlichen Grenzgebiete und Naturphilosophie und wurde 1927 a. o. Professor. Obwohl er zeit

seines Lebens die naturphilosophischen Probleme mit großem Interesse verfolgte, galt seine besondere Neigung und Fähigkeit den exakten Naturwissenschaften. So folgte er gerne einer Berufung an die Vatikanische Sternwarte, wo er ein astrophysikalisches Laboratorium einrichten sollte, mit der speziellen Aufgabe, sich zunächst der spektrochemischen Analyse der Meteoriten zu widmen, deren ansehnliche Sammlung *Marquis de Mauroy* der Vatikanischen Sternwarte geschenkt hatte. Papst *Pius XI.* bewilligte großzügig die Mittel, und so entstand 1933/34 unter P. *Gatterers* Leitung eines der bestausgestatteten spektrochemischen Laboratorien, dem er bis an sein Lebensende vorstand.

Schon bei den ersten Analysen der Meteoriten erwies es sich als wünschenswert, genaue photographische Tafeln der Spektren des Eisens und der anderen in Frage kommenden Elemente zur Hand zu haben. So entstanden die Spektralatlanten (die beiden Eisenspektren und der dreibändige Atlas der letzten Linien), die dann im Laufe der Jahre ihren Weg in die meisten spektroskopischen Laboratorien der ganzen Welt fanden und den Ruf des Laboratoriums und seines Leiters begründeten. Sie erwiesen sich als so nützlich, daß die Kommission für Sternspektren der Internationalen Astronomischen Union auf der Tagung in Zürich 1948 an P. *Gatterer* mit der Aufforderung herantrat, ähnliche Atlanten der Molekülspektren von astrophysikalischem Interesse herzustellen, besonders da es ihm gelungen war, mit Hilfe der sogenannten Kohleflamme Bandenspektren ohne störende Atomlinien zu erhalten.

Seine Versuche, neue Anregungsarten zu finden, führten ihn unter anderem zu einer guten Methode, auch Halogene und andere Nichtmetalle mittels Hochfrequenz der Spektralanalyse zugänglich zu machen.

Auf seine Anregung hin wurde 1938 die internationale Zeitschrift „*Spectrochimica Acta*“ ins Leben gerufen, deren erstes Heft dank der Energie der Leitung des Springer-Verlages, Berlin, bald darauf erscheinen konnte. P. *Gatterer* war von Anfang an Mitherausgeber und während der schwierigen Jahre 1947 bis 1949 sogar Hauptredakteur und Verleger für den 3. Band der Zeitschrift, der in der Vatikanstadt veröffentlicht wurde. Später konnte die Zeitschrift wieder an einen wissenschaftlichen Verlag, und zwar die Pergamon Press in London, abgegeben werden.

Das Laboratorium war seit Anbeginn auf rein spektrochemische Arbeiten eingestellt und P. *Gatterer* sorgte dafür, daß es in dieser Beziehung ständig auf der Höhe blieb, so daß sich schon bald Gäste einfanden, die sich hier in die Spektrochemie einführen lassen oder sich darin vervollkommnen wollten. Trotz seiner vielen eigenen Arbeiten half P. *Gatterer* gerne, soweit es immer möglich war.

P. *Gatterer* war Mitglied verschiedener wissenschaftlicher Vereinigungen, vor allem der Päpstlichen Akademie der Wissenschaften. Die Vereinigung französischer Spektrochemiker „Groupement pour l'avancement des

méthodes d'analyse spectrographiques" ernannte ihn zum Ehrenmitglied und die italienische spektroskopische Vereinigung im Rahmen der Associazione Italiana di Metallurgia machte ihn zum Ehrenpräsidenten, nachdem er die eigentliche Präsidentschaft wegen seiner eigenen zahlreichen Arbeiten nicht annehmen konnte und wollte. Auch der Österreichischen Gesellschaft für Mikrochemie gehörte er an.

Der Höhepunkt in seinem wissenschaftlichen Leben war es wohl, als die Joint Commission for Spectroscopy, die Spezialisten aus der Internationalen Astronomischen Union und aus der Internationalen Union für reine und angewandte Physik vereint und deren Mitglied P. *Gatterer* war, anläßlich des Internationalen Astronomischen Kongresses in Rom 1952 eine ihrer Sitzungen nach Castel Gandolfo verlegte und mit besonderer Befriedigung sein Laboratorium besuchte.

Nach diesem Kongreß versuchte er mit schon schwindenden Kräften, seine Arbeit, die Aufnahme der Bandenspektren, weiterzuführen. Zu Weihnachten fuhr er nach Innsbruck, um sich einmal gründlich untersuchen zu lassen. Man stellte ein Plasmocytom fest, verbunden mit hochgradiger Anämie. Einige Bluttransfusionen führten anfänglich eine Besserung herbei, so daß er hoffte, Mitte Februar wieder in sein Laboratorium zurückkehren zu können. Ein plötzliches Versagen der Nierentätigkeit führte aber in wenigen Tagen, am 17. Februar 1953, den Tod herbei.

Mit P. *Gatterer* verliert die Wissenschaft, besonders die Spektrochemie, einen begeisterten, unermüdlichen und aufgeschlossenen Meister, das Astrophysikalische Laboratorium seinen Schöpfer und Gestalter. Seine Arbeiten werden in seinem Geiste weitergeführt werden; das Programm ist durch ihn noch auf manche Jahre festgelegt, doch das Fehlen seiner reichen Erfahrung und experimentellen Kunst wird noch lange stark fühlbar bleiben.

1932 erschien die erste Veröffentlichung P. *Gatterer*s auf spektrochemischem Gebiet. Die 20 Jahre bis zu seinem Tode brachten eine außerordentliche Entwicklung dieses Fachgebietes. Trotz schwerer Behinderung durch Krankheit und körperliche Gebrechen hat P. *Gatterer* daran wesentlichen Anteil. Sein Name wird mit der Spektrochemie für immer verbunden bleiben. Für diejenigen, die ihn persönlich kannten, wird seine unermüdliche Hingabe an die Wissenschaft und nicht zuletzt seine persönliche Güte immer ein Vorbild sein.

P. *E. Salpeter* S. J. — Castel Gandolfo.

Contribution from the Department of Chemistry, New York University, New York.

# Determination of Phosphorus in Organic Compounds: A New Micro Procedure.

By

**T. S. Ma** and **John D. McKinley, Jr.**

With 6 Figures.

*(Received January 12, 1953.)*

In view of the increasing use of organic phosphorus compounds in agriculture, medicine, and industry[1], it was deemed desirable to review the micro procedures for the determination of phosphorus in search of a simple, rapid, and reliable method. Three such procedures have been described in the literature[2]. In all of them, the organic matter is first destroyed, usually by wet oxidation. The phosphoric acid formed is then converted to phosphomolybdate which is either (1) weighed, or (2) dissolved in standard alkali and titrated, or (3) reduced to molybdenum blue and photometrically measured. The titrimetric method is not favored because it involves several steps and is time consuming. The gravimetric procedure, first described by *Lieb* and *Wintersteiner*[3] is recommended by the current laboratory manuals on organic microanalysis[2,4]. While this method offers a favorably large conversion factor for the determination of phosphorus, it suffers from the disadvantages that (a) the precipitation requires many hours and (b) a standard procedure has to be strictly adhered to because of the empirical conversion factor. *Tsuzuki* and *Miwa*[5] claim that the factor given in the literature is about 1% too high.

The molybdenum blue method has found application in the microchemical field where the amount of phosphorus present in the sample is extremely small. *Horecker*, *Ma*, and *Haas*[6] have described a procedure for the determination of microgram quantities of phosphorus using the spectrophotometer, and *Roth*[7] has proposed a procedure using the stepphotometer. When this colorimetric method is applied to the determina-

tion of phosphorus in three or more milligrams of organic compounds which contain from 5 to 30% phosphorus, the color is too intense for accurate measurement unless the final solution is diluted to a very large volume. Other undesirable features of the method are: (a) the color is not very stable, and (b) the reducing agents employed for the development of the blue color cannot be kept for longer than a few days.

The colorimetric method of analysis is attractive, however, because of its rapidity and simplicity, and it is of particular value for series determinations. It occurred to the authors that the yellow color produced on mixing ammonium vanadate, molybdate, and phosphate would be suitable for micro determination of phosphorus in organic compounds. The colored complex, known as ammonium phosphovanadomolybdate or molybdivanadophosphoric acid, was first described by *Mission*[8]. It has been used for the macro determination of phosphorus in steel[9], iron ore[10], limestone[11,12], phosphate rock[13], plants[14], foods and fertilizers[15], agricultural materials[16], and organic phosphates[17,18]. *Kitson* and *Mellon*[19] have studied the effect of temperature and acidity on the color as well as the influence of the presence of various ions and have come to the conclusion that this complex has several advantages over molybdenum blue for the determination of phosphorus in steels.

Organic phosphorus has been converted to phosphoric acid by digestion with hydriodic acid, sulfuric-perchloric or sulfuric-nitric acid mixture, and by alkali fusion[17]. The last is tedious. *Simmons* and *Robertson*[18] reported that the hydriodic acid method was unreliable and recommended the use of perchloric acid. While the latter is an effective oxidizing agent, it is to be avoided because of danger of explosion. The authors have found that digestion with a mixture of sulfuric and nitric acids is sufficient for the decomposition of various types of organic phosphorus compounds.

### Absorption Characteristics of Ammonium Phosphovanadomolybdate.

In order to test the suitability of the yellow color of ammonium phosphovanadomolybdate for the micro determination of phosphorus in organic compounds, the absorption characteristics of the complex were studied in solutions containing 0.1 to 3.0 mg of phosphorus per 100 ml. This volume was chosen because it is the most practical to handle. Thorough mixing can be easily and quickly attained by the use of the 100-ml volumetric flask, which also provides enough solution for visual comparison if desired.

The colored complex is produced by mixing a solution containing an accurately measured quantity of phosphate ion with the ammonium molybdate and ammonium vanadate reagents according to the procedure

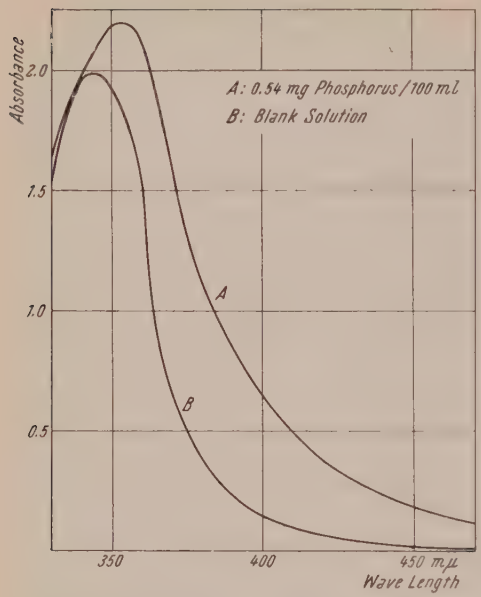



Fig. 1. Absorption Spectra of Phosphorus Complex and Blank Solution.

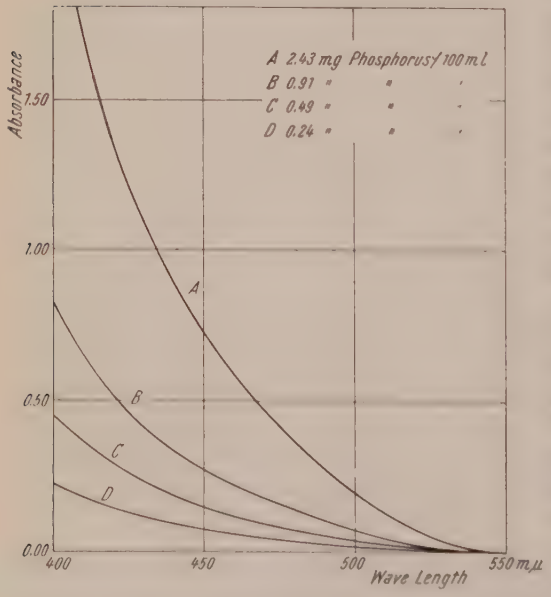



Fig. 2. Absorbance of Complex Measured against Blank.

described below. Fig. 1 shows the absorption curve of the complex compared with that of the blank. It will be noted that the two curves show maximum spread at 410 mμ. This wave length was therefore chosen for the measurement of absorbance ($A = -\log T$) in the determination of phosphorus. Higher wave lengths have been recommended for the determination of phosphorus in iron and steel to avoid the interference by the color of ferric iron[11]. This consideration is of little consequence in the analysis of organic phosphorus compounds.

Since a solution of the reagents alone, in the absence of any phosphorus, possesses a very faint yellow tint, it is advisable to compare samples with a blank rather than with distilled water. Fig. 2 presents a set of absorption curves at varying concentrations of phosphorus, using the blank as zero reference level.

The absorption behavior of the colored complex is shown to follow the *Beer-Lambert* law between 0.1 and 3.0 mg of phosphorus per 100 ml when measured at 410 mμ and at 430 mμ (Fig. 3). Curve *A* in Fig. 3 is the standard curve used for the determination of phosphorus

reported in this communication. It may be mentioned that the points along the curve include all data obtained with solutions prepared at different times during a period of about a month while using the same phosphate standard solution and reagents; no measurement has been discarded. The absorption was measured at room temperature which varied to the extent of 3° C. It appears that the reagents are quite stable and that the color is not very sensitive to temperature variations.

*Kitson* and *Mellon*[19] report that the yellow

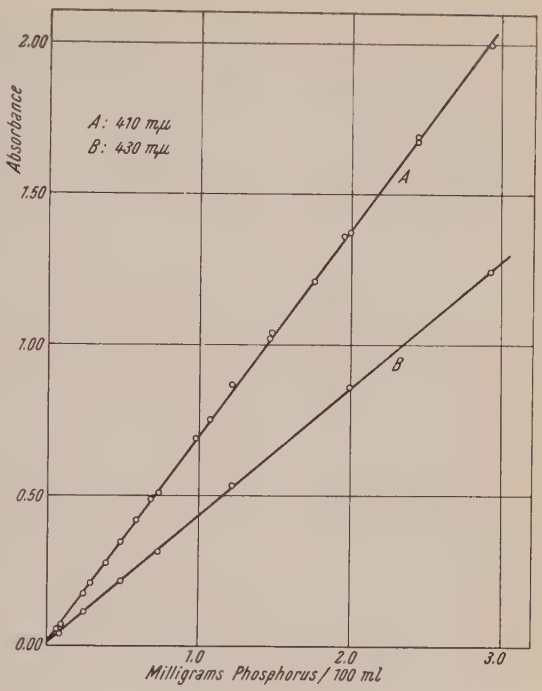



Fig. 3. Standard Curves.

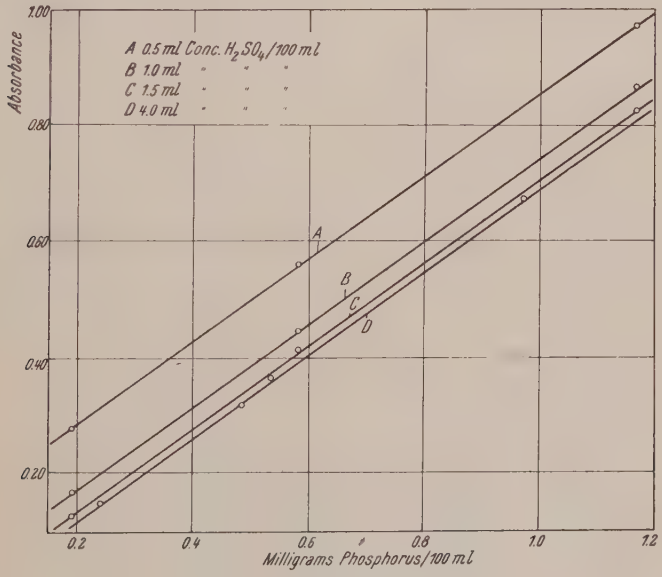



Fig. 4. Effect of Acid Strength.

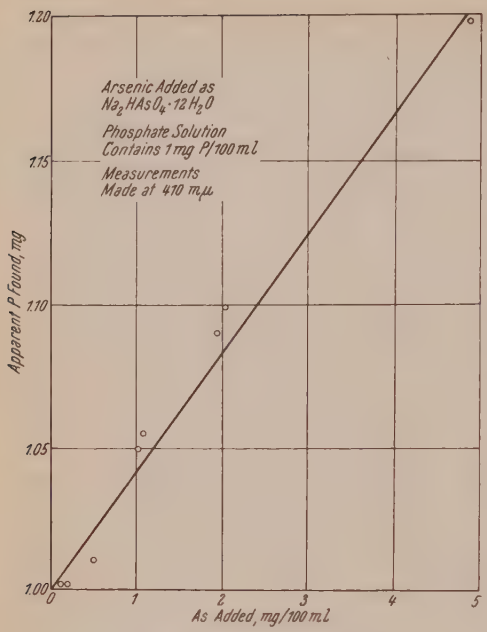



Fig. 5. Effect of Arsenic on Phosphorus Determination.

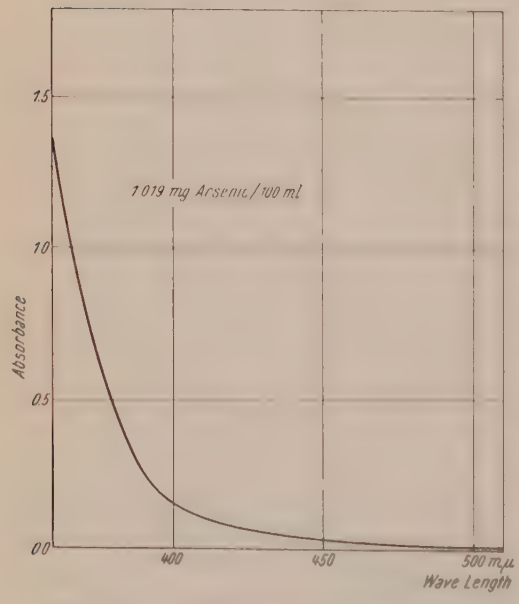



Fig. 6. Absorption Spectrum of Arsenic Complex.

color is affected by the concentration of acid in the solution; they recommend 0.5 N acid as the optimum concentration. Since acid digestion is employed for the decomposition of organic phosphorus compounds, it was necessary to determine the influence of the acid concentration in the final solution. Fig. 4 shows the absorbance of solutions at various acid concentrations as compared with that of the adopted procedure (curve *C*). It can be seen that the intensity of the color increases rapidly when the acid concentration falls below 1.0 ml of concentrated sulfuric acid per 100 ml of solution, but the color changes only slightly when more than 1.5 ml of concentrated sulfuric acid is present. On the other hand, the authors have observed that the development of the color is retarded by the presence of large quantities of sulfuric acid. Since 1.5 ml of concentrated sulfuric acid provides a suitable volume of digestion medium for microanalysis (2 to 10 mg sample), this quantity is used in the recommended procedure.

Arsenic is one of the common interfering substances in the determination of phosphorus, and it is general practice to remove it beforehand[2]. The authors have

found, however, that removal of small quantities of arsenic is not necessary when the ammonium vanadophosphomolybdate method is used. A positive error of about 5% is incurred when equal amounts of arsenic and phosphorus are present in the solution; the error increases to about 20% when there is five times as much arsenic as phosphorus, Fig. 5. The absorption characteristics of the arsenic complex are given in Fig. 6.

## Recommended Procedure.

*Reagents:*

*Standard phosphate solution.* The standard solution containing 0.500 mg of phosphorus per ml is prepared by dissolving 2.1315 g of pure diammonium-hydrogen phosphate or 2.196 g of pure potassium-dihydrogen phosphate in a 1-liter volumetric flask and diluting to the mark.

*Ammonium vanadate solution containing 0.20% vanadate.* This is prepared by cautiously adding to 500 ml of boiling distilled water first, 2.35 g of ammonium metavanadate, $NH_4VO_3$, C. P., and then 100 ml of dilute sulfuric acid (1:12). After cooling, the solution is made up to 1 liter.

*Ammonium molybdate solution containing 10% $MoO_3$.* This is obtained by dissolving 122 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, reagent grade, in 880 ml of distilled water.

*Concentrated sulfuric acid,* C. P.

*Concentrated nitric acid,* C. P.

The vanadate, molybdate and phosphate solutions are preferably dispensed from automatic burets. All solutions have been kept in closed bottles for 4 months with no sign of deterioration.

*Preparation of the Standard Curve.* Ten aliquot portions of the standard phosphate solution, covering the range from 0.10 to 2.00 mg phosphorus, are measured into 100-ml volumetric flasks from a micro buret which may be accurately read to 0.005 ml. A blank is started at the same time. The aliquots are diluted to 65 ml and treated with 1.4 ml of concentrated sulfuric acid. Then 10 ml of the vanadate solution is added slowly, with continuous swirling, to each batch. This is followed by 10 ml of the molybdate solution. Finally, the flasks are filled to the mark with distilled water. After standing for 30 minutes, the yellow color is compared with that of the blank. The measurements reported in this communication were made with a Beckman spectrophotometer model DU, at 410 m$\mu$ with slit width of 1.0 mm and the solutions in 1-cm matched Corex cells. The color intensity remains constant for many days. A straight line is obtained by plotting absorbance ($A = -\log T$) against mg of phosphorus

in the solution, and from the slope and intercept of this line an equation can be derived of the form

$$w = \alpha A + \beta$$

which gives the weight $w$ of phosphorus in terms of absorbance $A$. Curve $A$ in Fig. 3 is represented by

$$w = 1.4368\, A - 0.0129.$$

*Determination of phosphorus.* From 3 to 10 mg of the compound, corresponding to 0.2—1.5 mg phosphorus, is weighed in a charging tube and transferred into a dry 10-ml Kjeldahl digestion flask. After introducing 1.5 ml of concentrated sulfuric acid, 4 drops (0.2 ml) of concentrated nitric acid are added. The flask is heated gently on the digestion rack until the reaction subsides. After cooling, 2 more drops of concentrated nitric acid are added, and the flask is again heated with a medium flame until the solution is clear and sulfur trioxide fumes are evolved (20 to 30 minutes). The solution is cooled, diluted to about 10 ml, and then transferred with several rinsings to a 100-ml volumetric flask. The color is developed and measured as in the preparation of the standard curve. The amount of phosphorus is obtained either from the graph or with the use of the equation.

## Discussion of Results.

The analytical results of 19 samples representing several different classes of organic phosphorus compounds are listed in Table I. Considering the structures of the compounds, one may conclude that cleavage of the phosphorus-carbon or phosphorus-nitrogen bond is accomplished by heating with the sulfuric-nitric acid mixture, and that destruction of the organic fragment of alkyl, phenyl, or naphthyl phosphate is complete under the conditions of the digestion. The excellent results shown by triphenyl phosphine and phenyl phosphorous acid indicate that trivalent phosphorus is quantitatively oxidized to the pentavalent state by the digestion mixture employed.

The recommended procedure gives results of about the same degree of accuracy as the gravimetric method, but surpasses the latter in speed and simplicity. The stability of the reagents and of the colored complex offers many advantages: a series of digestions may be carried out simultaneously, the color developed at a convenient time, and measurements performed when all solutions are ready.

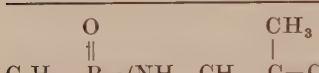
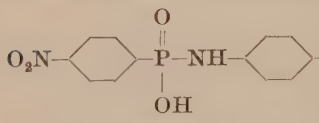
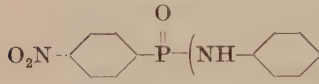
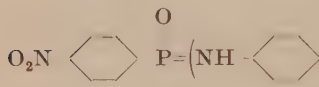
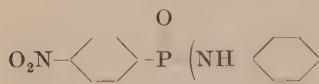
## Acknowledgment.

The authors wish to thank Dr. *A. D. F. Toy* of Victor Chemical Works, Chicago Heights, Ill., for a gift of organic phosphorus compounds.

Table I. Phosphorus Determination.

| Compound | Sample Taken mg | Phosphorus, % | | Difference |
|---|---|---|---|---|
| | | Found | Theory | |
| $(C_6H_5)_3 \equiv P$ | 7.542 | 11.72 | 11.81 | — 0.09 |
| $C_6H_5—P(=O)(OH)_2$ | 6.532 | 21.77 | 21.80 | — 0.03 |
| $C_6H_5O—P(=O)(ONa)_2$ | 4.451 | 14.30 | 14.20 | + 0.10 |
| $(C_2H_5O)_2=P(=O)—O—C_6H_2Cl_3$ (Cl Cl / Cl Cl) | 9.659 | 7.57 | 7.70 | — 0.13 |
| $C_6H_5—P(=O)(OH)_2$ | 6.030 | 19.35 | 19.59 | — 0.24 |
| $C_6H_5—P(=O)(ONa)_2$ | 5.816 | 15.12 | 15.33 | — 0.21 |
| $O_2N—C_6H_4—P(=O)(OH)_2$ | 7.271 | 15.43 | 15.25 | + 0.18 |
| $(C_{10}H_7O)_3 \equiv P=O$ | 6.042 | 6.42 | 6.50 | — 0.08 |
| $C_6H_5—CH=CH—P(=O)(OC_6H_5)_2$ | 7.670 | 9.20 | 9.21 | — 0.01 |
| $(C_2H_5O)_2=P(=O)—NH—C_6H_4—NO_2$ | 6.579 | 11.29 | 11.30 | — 0.01 |
| $O_2N—C_6H_4—P(=O)(NH—C_6H_4—Cl)_2$ | 5.661 | 7.01 | 7.34 | — 0.33 |
| $O_2N—C_6H_4—P(=O)(OH)—NH—C_6H_4—OCH_3$ | 6.339 | 10.08 | 10.06 | + 0.02 |
| $O_2N—C_6H_4—P(=O)(NH—C_6H_5)_2$ | 5.859 | 8.77 | 8.77 | 0.00 |
| $O_2N—C_6H_4—P(=O)(OH)—NH—C_6H_4—C_6H_5$ | 8.235 | 8.49 | 8.74 | — 0.25 |

Table I. Phosphorus Determination (Continued).

| Compound | Sample Taken mg | Phosphorus, % Found | Phosphorus, % Theory | Difference |
|---|---|---|---|---|
|  | 5.727 | 11.49 | 11.72 | — 0.23 |
|  | 5.824 | 10.19 | 9.91 | + 0.28 |
|  | 4.725 | 7.12 | 7.50 | — 0.38 |
|  | 5.835 | 6.80 | 6.99 | — 0.19 |
|  | 5.154 | 8.25 | 8.13 | + 0.12 |
| | | | Standard deviation... | ± 0.19 |


## Summary.

A new micro procedure for the determination of phosphorus in organic compounds has been developed. It is based on the yellow complex produced by mixing ammonium vanadate, molybdate, and phosphate. The procedure is rapid, simple, and suited for series determinations; the reagents and the colored compounds are stable. A precision of ± 0.2% phosphorus is obtained with samples of 3 to 10 mg weight.

## Zusammenfassung.

Das beschriebene Mikroverfahren für die Phosphorbestimmung in organischen Substanzen beruht auf der photometrischen Auswertung des gelben Komplexes mit Vanadat und Molybdat. Es ist einfach, schnell, und für Serienbestimmungen geeignet. Die dafür nötigen Reagenzien sind gut haltbar, die gefärbte Verbindung ist beständig. Eine Genauigkeit von ± 0.2% Phosphor wird mit Probemengen von 3 bis 10 mg erhalten.

## Résumé.

On présente un micro-procédé de dosage du phosphore dans des composés organiques. Il repose sur le complexe jaune produit en mélangeant des vanadate, molybdate et phosphate d'ammonium. Le procédé est rapide, simple et convenable pour les dosages en série. Les réactifs et les composés colorés sont stables. Une précision de ± 0,2% sur le phosphore est obtenue avec des échantillons allant de 3 à 10 mg.

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# Entwicklung und Einleitung von Gasen in kleine Flüssigkeitsmengen.

Von

**Herbert Weisz.**

Mit 1 Abbildung.

*(Eingelangt am 27. Januar 1953.)*

Bei der Durchführung mikroanalytischer Arbeiten ergibt sich häufig die Notwendigkeit, Gase in sehr kleine Flüssigkeitsmengen einzuleiten[1, 3]. In unserem Institut haben wir seit längerer Zeit einen Apparat in Verwendung, der sich bestens bewährt hat und der hier in aller Kürze beschrieben sei (Abb. 1):

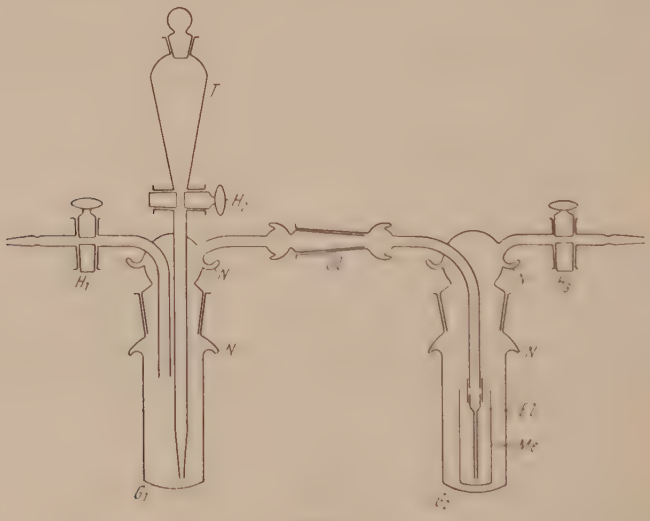

Abb. 1.

In das Gasentwicklungsgefäß $G_1$, das 65 mm hoch ist und 25 mm Durchmesser hat, führen durch eine Schliffkappe ein Zuleitungsrohr mit

Hahn $H_1$, ein Tropftrichter $T$ und ein Überleitungsrohr $Ül$; in das gleichdimensionierte Gaseinleitungsgefäß $G_2$ münden das Gasüberleitungsrohr und das Gasabsaugrohr mit Hahn $H_3$. Das Überleitungsrohr ist zwecks leichterer Reinigung mit einem Schliff versehen; außerdem ist am Überleitungsrohr eine kugelförmige Erweiterung angebracht, die mit Watte gefüllt wird, um eventuell mitgerissene Flüssigkeitstropfen zurückzuhalten. An das Ende des Überleitungsrohres, das in das Gaseinleitungsgefäß ragt, ist mit einem Kautschukschlauch ein Einleiteröhrchen *El* Glas an Glas befestigt; wir halten verschieden lange Einleitungsspitzen vorrätig, um je nach der Art des Fällungsgefäßes und der Flüssigkeitsmenge die jeweils optimale Eintauchtiefe zu erzielen. Außerdem ist die Reinigung der ganzen Apparatur durch die Verwendung auswechselbarer Einleiteröhrchen sehr erleichtert, da ja nur diese gereinigt werden müssen. Im Gaseinleitungsgefäß endlich ist das eigentliche Fällungsgefäß, beispielsweise eine Mikroeprouvette *Me*, untergebracht. Die ganze Apparatur steht in einem Aluminiumblock geeigneter Dimension, dessen Bohrungen mit Asbest ausgekleidet sind; außerdem trägt er eine Bohrung zur Aufnahme eines Thermometers unmittelbar neben dem Gaseinleitungsgefäß, da man durch Erwärmen des Aluminiumblockes — die ganze Apparatur ist aus Jenaer Glas gefertigt — die Möglichkeit hat, Fällung und Gasentwicklung auch bei höherer Temperatur vorzunehmen.

Die Arbeitsweise des Apparates sei am Beispiel einer Fällung mit Schwefelwasserstoff kurz beschrieben:

In das Gasentwicklungsgefäß wird eine ausreichende Menge Zinksulfid eingebracht, in das Einleitungsgefäß die Mikroeprouvette mit dem Probetropfen, an das Überleitungsrohr wird ein passendes Einleiteröhrchen angesteckt, der Apparat geschlossen, sodann in den Tropftrichter Salzsäure (1:1) gegeben. Vor die Zuleitung $H_1$ wird ein Sicherheitsröhrchen mit Watte zur Luftfiltration geschaltet, am Gasabsaugrohr unter Zwischenschaltung einer Sicherheitsflasche ganz schwach mittels einer Wasserstrahlpumpe gesaugt. Alle Hähne sind vorerst geschlossen. $H_2$ und $H_3$ werden ein wenig geöffnet, Salzsäure einfließen gelassen, $H_2$ sofort wieder geschlossen. Hernach wird $H_1$ so weit geöffnet, daß ein ganz schwacher Luftstrom durch die Apparatur streicht, der als Transportmedium für den Schwefelwasserstoff dient. Der durch die Probelösung hindurchperlende Gasstrom bewirkt eine gründliche Durchmischung. Es ist auch möglich, einen inerten Gasstrom durchzuleiten, wenn man bei Zuleitungsrohr $H_1$ einen Gasbehälter mit dem entsprechenden Gas anschließt. In diesem Falle erübrigt es sich natürlich, bei $H_3$ zu saugen. Die Fällung mit Schwefelwasserstoff kann auch bei einem geringen Überdruck erfolgen, wenn alle Hähne geschlossen sind, die Spiralfedern (zwischen den Nasen $N$ angebracht) sorgen für einen festen Verschluß der Apparatur. Nach der meist in wenigen Minuten beendeten

Fällung leitet man noch einige Zeit Luft oder sonst einen Gasstrom durch, um allen Schwefelwasserstoff zu entfernen; hernach kann der Apparat geöffnet werden, ohne daß Schwefelwasserstoff in die Laboratoriumsluft entweichen kann. Außer zu Schwefelwasserstofffällungen wenden wir in unserem Institut das Gerätchen vor allem zu Oxydationen mit Bromluft, besonders bei der Lösung von Sulfidniederschlägen an. In das Gasentwicklungsgefäß wird Bromwasser bzw. Brom eingebracht oder Kaliumbromid und Kaliumbromat und durch den Tropftrichter Salzsäure zufließen gelassen. Wie schon eingangs erwähnt, lassen sich natürlich in sinngemäßer Variation eine Anzahl von Reaktionen auf einfachste Weise mit dem handlichen Gerät durchführen.

## Zusammenfassung.

Es wird eine Apparatur zur Entwicklung von Schwefelwasserstoff und anderen Gasen und deren Einleitung in kleine Flüssigkeitsmengen — bis zu 1 Tropfen — beschrieben. Die gasförmigen Reagenzien können bei höherer Temperatur, bei Überdruck sowie in Verdünnung durch einen indifferenten Gasstrom angewendet werden, ohne in die Außenluft zu gelangen.

## Summary.

A description is given of an apparatus for the evolution of hydrogen sulfide and other gases and their passage into small volumes of liquid down to one drop. The gaseous reagents can be employed at an elevated temperature, under pressure and also diluted by an indifferent stream of gas, without coming into the outer atmosphere.

## Résumé.

On décrit un appareil à dégagement d'hydrogène sulfuré et autres gaz ainsi que l'introduction dans de petites quantités de fluide – jusqu'à une goutte –. Les réactifs gazeux peuvent être utilisés à plus haute température, en surpression ou dilués dans un courant de gaz indifférent sans s'échapper dans l'air extérieur.

## Literatur.

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# The Determination of Glycidic Esters*.

By

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With 1 Figure.

*(Received January 29, 1953.)*

In the course of investigations regarding the chemistry of glycidic esters[1], it became necessary to have available a method suitable for determining the amount of glycidic esters present in a reaction mixture.

A literature search had shown that there are no recorded methods specific for epoxy esters. *Siggia* had reported[2] a procedure for the determination of epoxy compounds and substituted epoxy compounds in which the substituents were either hydrogen or alkyl. However his method was not applicable to glycidic esters since two functional groups are present in these compounds, the ethylene oxide group and the ester. Both of these react with the solution of calcium chloride in hydrochloric acid used by *Siggia*. The reaction with glycidic esters gives not only the expected chlorohydrin, but also the calcium salt of the corresponding acid. The standard base employed not only neutralizes the excess acid, but also reacts with some of the calcium salt. Attempts to determine a blank for this system were of no avail as it was impossible even to reproduce the error.

*Darzens*[3] has reported that glycidic esters react quantitatively with hydrogen iodide to give an acrylic ester and iodine. Since glycidic esters are either colorless or, at most, pale yellow in color, the occurence of the red color due to the liberated iodine gives immediate evidence of the presence of this type of compound. Determination of the amount of liberated iodine would also measure the amount of glycidate originally present.

* Communication No. 272. The data presented were taken from a part of the thesis of M. E. D., submitted to the Graduate School of Fordham University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

To use this reaction for the determination of glycidic esters it was necessary to have available either anhydrous hydrogen iodide or a generator of this gas. The two procedures for preparing anhydrous hydrogen iodide are that of *Bannow*[4], in which red phosphorus reacts with a solution of hydriodic acid and iodine, and the other, that of *Houben*[5], in which iodine reacts with tetralin to give hydrogen iodide and naphthalene.

The method of *Bannow*, while apparently very simple, was not suited. In this procedure a solution of iodine in hydriodic acid is dropped onto red phosphorus and the gas formed is then conducted to the test solution. However, the constant boiling hydriodic acid used is not saturated. Thus, when the first drops come in contact with the atmosphere of the generating flask, they will immediately dissolve some of the hydrogen iodide with resultant formation of a partial vacuum in the delivery line. This in turn draws the test solution back into the delivery tube or the trap, and the determination is lost.

In *Houben*'s method for preparing hydrogen iodide the gas is generated continuously in a closed system and with no possibility of a change in pressure in the system. After the hydrogen iodide from the generating flask has passed through three chilled traps to remove any iodine, tetralin, or moisture carried over from the generator, it is conducted to the reaction flask containing a weighed sample of ester dissolved in ether. Upon completion of the reaction, a measured amount of standard sodium thiosulfate is added and the excess thiosulfate then back-titrated with iodine. The amount of glycidate present can be calculated from the amount of thiosulfate used by means of the following equation:

$$12.7\,(A - B) \cdot N \cdot M/254\,S = \text{percentage of glycidate} \qquad (1)$$

where $A$ is the volume of thiosulfate originally added; $B$ the volume of iodine needed to react with the excess thiosulfate; $N$ is the normality of the thiosulfate, from 0.1 $N$ to 0.01 $N$; $M$ is the molecular weight of the glycidate; and $S$ is the weight of the sample.

It is necessary to use a sample weighing 10 to 15 milligrams, since a larger sample requires a longer contact time. This would lead to abnormally high results due to the light-sensitivity of the hydrogen iodide.

This procedure, however, suffers from two disadvantages. First, it is slightly cumbersome and second, it requires cleaning out the entire apparatus between runs because of the decomposition of the hydrogen iodide. The latter is not important when isolated determinations are carried out, but when a series of analyses are necessary, much more time is spent assembling the apparatus than in carrying out the analyses. Attempts were therefore made to streamline the procedure. In his report on the action of hydrogen iodide upon glycidic esters, *Darzens*[3] mentioned that the entire reaction mixture must be free of moisture.

Since water is one of the products of the reaction, the presence of outside moisture can affect the equilibrium and stop the reaction at the iodohydrin step. We thought that if constant boiling hydriodic acid (sp. gr. 1.54, 54%) were used with a small sample, approximately 0.01 of the acid would be necessary to give the required amount of hydrogen iodide. The small amount of excess water present in this 0.01 ml might be taken care of by the addition of a drying agent, and a series of analyses could be run consecutively. Our assumption proved incorrect. While this procedure never satisfactorily accounted for the amount of glycidate known to be present, the amount of loss was always constant. By inserting the factor 1.37 in equation (1), which applies to the longer determination, the correct percentage of the ester could be calculated using the shorter method of analysis.

## Experimental.

*Preparation of Hydrogen Iodide.* In a 2-liter three-necked round-bottom flask (Fig. 1, Flask *A*), fitted with a water condenser (*B*), were placed 20 g of tetralin. The top of the condenser was connected to a 500-ml flask (*C*) which had been immersed in an ice-salt bath. After

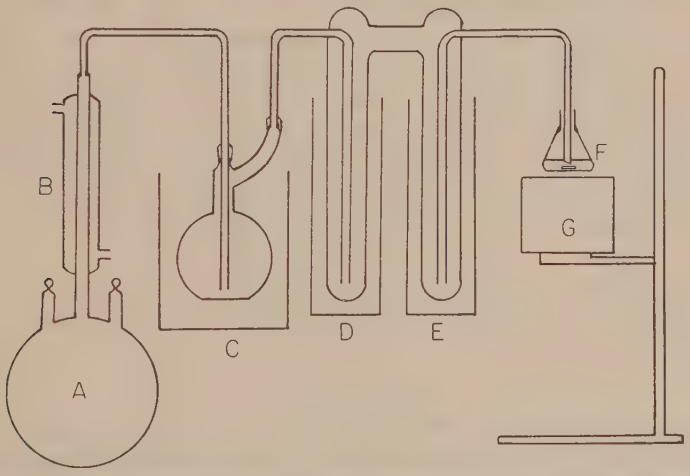


Fig. 1. Determination of Glycidic Esters. *A*, hydrogen iodide generator; *C*, *D*, *E*, cooled traps; *F*, reaction Flask; G, magnetic stirrer.

leaving the flask *C*, the gas stream was then conducted through two traps (*D*, *E*) also immersed in an ice-salt bath. Both of these traps were so designed that there was an alternate slight contraction and expansion of the gas stream. From the aperture in the last trap, the hydrogen iodide was conducted into the reaction flask (*F*). The tetralin in flask *A* was brought to a gentle boil by means of a Glas-Col electric heating

mantle, and 20 g of iodine were added in portions but as rapidly as possible. After allowing a few seconds for sweeping out the apparatus, the reaction flask was connected.

*Determination of the Glycidic Ester.* One drop of the glycidic ester (approximately 10 to 15 mg) was weighed out in either a sealed ampoule or a small weighing bottle. This was placed in the reaction flask *F*, a 125-ml Erlenmeyer flask, and covered with approximately 25 to 30 ml of anhydrous ether. The hydrogen iodide was allowed to pass through this solution for about five minutes or until a maximum red coloration was obtained. During this period the solution was stirred as vigorously as possible by means of a magnetic stirring element (*G*). The flask was then removed from the train and 8 to 9 ml of 0.1 *N* sodium thiosulfate [*A* of equation (1)] was added from the buret. The solution was stirred again and a few crystals of potassium iodide were added. Stirring was continued until the ether layer was colorless, at which time the flask was placed in a warm water bath and the ether evaporated off as gently as possible. The flask was then cooled, starch indicator was added, and the excess thiosulfate titrated with standard iodine solution. The volume of iodine used is *B* in equation (1).

*Determination of the Glycidic Ester (Short Method).* Into a stoppered 125-ml Erlenmeyer flask was placed a sample of 10 to 15 mg, weighed out as described above, 25 ml of anhydrous ether, and 0.5 g of anhydrous sodium sulfate. To this mixture was added 0.15 ml of colorless hydriodic acid (sp. gr. 1.54, 57%) and the resulting solution stirred as vigorously as possible by means of a magnetic stirring element. After a maximum red coloration had been obtained, the sodium thiosulfate was added and the determination finished as described above.

**Acknowledgement.**

This study was carried out under the auspices of the Office of Naval Research.

**Summary.**

A specific method for the quantitative estimation of glycidic esters utilizing the reaction between the epoxy group and anhydrous hydrogen iodide to give iodine, has been developed. A shorter method utilizing hydriodic acid (sp. gr. 1.54, 57%), while slightly inaccurate, and employing an empirical factor, is offered as a substitute for the former method which is more reliable but more complicated in manipulation.

**Zusammenfassung.**

Es wurde eine spezifische Methode zur quantitativen Bestimmung von Glycidyl-Estern beschrieben, die auf der Reaktion der Epoxygruppe mit wasserfreier Jodwasserstoffsäure beruht, bei der freies Jod entsteht. Ein

einfacheres Verfahren verwendet 57%ige Jodwasserstoffsäure vom spez. Gew. 1,54. Dieses ist zwar etwas ungenauer als die erste Methode, jedoch einfacher in der Ausführung.

**Résumé.**

Mise au point d'une méthode quantitative pour les esters glycidiques utilisant la réaction entre le groupe époxy et l'acide iodhydrique anhydre ce qui donne de l'iode. Une méthode plus rapide avec l'acide iodhydrique de densité 1,54 ou à 57% quoique moins précise est présentée comme remplacement en utilisant un facteur empirique de la première méthode qui est plus digne de confiance mais d'une manipulation plus compliquée.

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# Determination of Submicrogram Quantities of Osmium by Catalysis.

By

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With 3 Figures.

*(Received February 10, 1953.)*

The feasibility of determining minute amounts of osmium by its catalysis of the reaction between cerium(IV) and arsenic(III) was shown by *Ivan*[1] in a preliminary study more than ten years ago. *Shiokawa*[2] has also made use of the catalytic effect of osmium on various slow reactions for its determination. We have studied the Ce(IV)-As(III) method in greater detail, and find that it can be used to determine as little as 0.005 $\mu$g osmium at a dilution of $1:10^9$. The present work has been confined to the determination of osmium in solution. The sensitivity is so great that it should be possible to apply the method to the determination of osmium in sulfide, and possibly other minerals, if means of bringing osmium into solution can be devised. Application of the method to iron meteorites, which appear to contain a few parts per million of osmium, should involve no difficulties.

No catalytic method will be of general value in applied trace analysis unless the procedure provides for the separation of the element in question from other substances, even indifferent electrolytes which are likely to affect the rate of the catalyzed reaction. The extractability of osmium tetroxide by chloroform or carbon tetrachloride furnishes an ideal means of isolating osmium. The other elements strongly catalyzing the Ce(IV)-As(III) reaction are ruthenium and iodine. The organic solvent extraction effects a sharp separation of osmium from ruthenium if it is preceded by an oxidative treatment which converts osmium to the octavalent state while leaving ruthenium in a lower valence state. Iodide can be made harmless with silver.

* From a portion of the Ph. D. thesis of *R. D. Sauerbrunn*, 1952.

*Kinetics of the Osmium-Catalyzed Ce(IV)-As(III) Reaction.*

The effect of the concentration of Ce(IV) and of As(III) on the reaction rate in the presence of osmium (as $OsO_4$) was investigated. In one series of experiments, 1.00 ml of 0.005 *N* ceric ammonium sulfate in 1 *M* sulfuric acid was added all at once, by hypodermic syringe, to 4.00 ml of a mixture containing 1 ml of 6 *M* sulfuric acid and various amounts of arsenious oxide. Since *Beer*'s law holds, the extinction of the solution was obtained

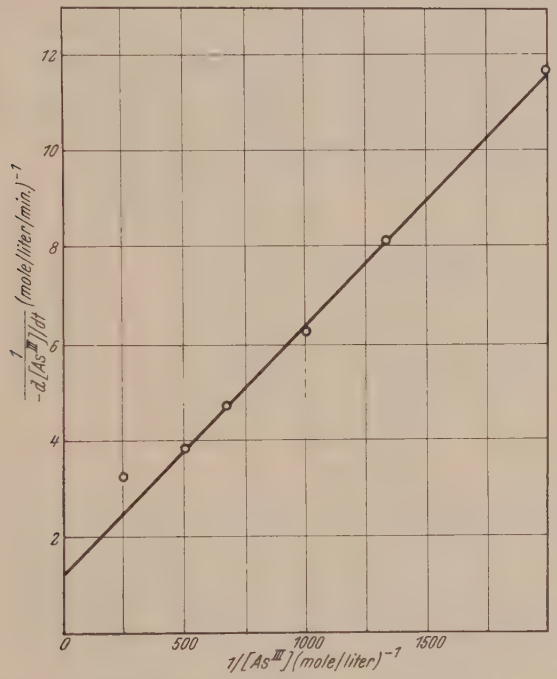


Fig. 1. Relation Between $-d[As^{III}]/dt$ and Concentration of As(III).

at intervals at 420 m$\mu$ in a Beckman model B spectrophotometer. In another series, 1.00 ml of 0.0025 *N* arsenious acid was added to 4.00 ml of a mixture containing various amounts of ceric ammonium sulfate, with the same sulfuric acid concentration as before, and the extinction was again obtained at suitable intervals.

The concentrations of Ce(IV) and As(III) were calculated from the extinction readings. For the early stage of the reaction, these concentrations were plotted as functions of time, and the initial slopes of the curves, listed in Table I, were found graphically. It is seen that the velocity of the catalyzed reaction is independent of the ceric concentration but increases with the arsenious acid concentration. Since the velocity

is not directly proportional to $[As^{III}]$, the reciprocal of the velocity was plotted against the reciprocal of $[As^{III}]$ at $[Os^{VIII}] = 0.001\,\mu g/ml$ (Fig. 1). This gives a linear relation and the rate equation may be represented by

$$-d\,[As^{III}]/dt = k\,f\,(Os)\,\frac{[As^{III}]}{k'' + [As^{III}]} \qquad (1)$$

where $f\,(Os) = [Os^{VIII}] + k'$.

When equation (1) is written in the form

$$\frac{1}{-d\,[As^{III}]/dt} = \frac{1}{k\,f\,(Os)} + \frac{k''}{k\,f\,(Os)\,[As^{III}]}$$

it is seen that the slope of the line in Fig. 1 is equal to $k''/k\,f\,(Os)$ and the intercept is equal to $1/k\,f\,(Os)$. From the values 1.2 for the intercept and $5.2 \cdot 10^{-3}$ for the slope, we find $k\,f\,(Os)_1 = 0.833$ and $k'' = 4.33 \cdot 10^{-3}$. Substitution of the latter value in equation (1) gives:

$$-d\,[As^{III}]/dt = k\,f\,(Os)\,\frac{[As^{III}]}{4.33 \times 10^{-3} + [As^{III}]}. \qquad (2)$$

In order to evaluate $k$ and $f\,(Os)$ in equation (2), we use the value 0.833 obtained for $k\,f\,(Os)_1$ when the osmium concentration is 0.001 $\mu$g per ml and calculate a value for $k\,f\,(Os)$ when the osmium concentration is 0.004 $\mu$g per ml, making use of the data in Table I:

$$0.833 = k\,(1 \cdot 10^{-3} + k'),$$
$$3.23 = k\,(4 \cdot 10^{-3} + k').$$

Table I. Initial Velocity of the Ce(IV)-As(III) Reaction at 25° C as Function of Ce(IV) and As (III) Concentrations. $[H_2SO_4] = 1.4$.

| $[As^{III}]_0$ $M$ | $[Ce^{IV}]_0$ $M$ | $[Os^{VIII}]$ $\mu g/ml$ | $-d\,[As^{III}]/dt$ moles liter$^{-1}$ min.$^{-1}$ | $-d\,[Ce^{IV}]/dt$ moles liter$^{-1}$ min.$^{-1}$ |
|---|---|---|---|---|
| $5.0 \cdot 10^{-4}$ | $1.0 \cdot 10^{-3}$ | 0.001 | 0.086 | 0.172 |
| $7.5 \cdot 10^{-4}$ | $1.0 \cdot 10^{-3}$ | 0.001 | 0.123 | 0.245 |
| $1.0 \cdot 10^{-3}$ | $1.0 \cdot 10^{-3}$ | 0.001 | 0.160 | 0.320 |
| $1.5 \cdot 10^{-3}$ | $1.0 \cdot 10^{-3}$ | 0.001 | 0.213 | 0.427 |
| $2.0 \cdot 10^{-3}$ | $1.0 \cdot 10^{-3}$ | 0.001 | 0.261 | 0.523 |
| $4.0 \cdot 10^{-3}$ | $1.0 \cdot 10^{-3}$ | 0.001 | 0.310 | 0.625 |
| $2.5 \cdot 10^{-4}$ | $5.0 \cdot 10^{-4}$ | 0.004 | 0.176 | 0.351 |
| $2.5 \cdot 10^{-4}$ | $1.0 \cdot 10^{-3}$ | 0.004 | 0.176 | 0.353 |
| $2.5 \cdot 10^{-4}$ | $1.5 \cdot 10^{-3}$ | 0.004 | 0.176 | 0.351 |
| $2.5 \cdot 10^{-4}$ | $2.0 \cdot 10^{-3}$ | 0.004 | 0.177 | 0.354 |

These equations furnish the values $k = 8.0 \cdot 10^2$ and $k' = 4 \cdot 10^{-5}$. Therefore equation (2) may be written:

$$-d\,[As^{III}]/dt = 8 \cdot 10^2\,([Os^{VIII}] + 4 \cdot 10^{-5})\,\frac{[As^{III}]}{4.3 \times 10^{-3} + [As^{III}]} \qquad (3)$$

where $[As^{III}]$ is expressed in moles/liter, time in minutes, and $[Os^{VIII}]$ in $\mu$g per ml.

From the analytical standpoint, several features of this expression for the rate are of interest. First, it appears that the reaction velocity is very nearly directly proportional to the osmium concentration. At very low osmium concentrations the correction factor $4 \cdot 10^{-5}$ (the order of magnitude rather than the precise value is of significance) plays an appreciable role. This factor represents the velocity in the absence of added osmium, which might be the velocity of the uncatalyzed reaction or that together with a velocity ascribable to traces of catalyst (e. g. iodine) in the reagents and water. Data will be presented later to show that this correction factor may have a value a little larger than found in these experiments. Second, although the reaction rate increases with the arsenious acid concentration, the increase is small above about 0.02 *M* or 0.04 *N*. This is the concentration of As(III) adopted for the general procedure described later.

The above results show that the slow step in the catalyzed reaction is the reduction of Os(VIII) by As(III). The mechanism has not been elucidated.

*Measurement of Reaction Rate for Analytical Purposes.*

In the subsequent work to be described the rate of the catalyzed reaction was determined by finding the time required for some constant fraction of Ce(IV) to react with a given excess of arsenious acid. Two methods were used to obtain the "reaction time". One consisted in finding the time required to decrease the extinction of the yellow solution to a specified value, the other in finding the time needed until the solution reached a specified oxidation potential. The first method is commonly used in catalytic reactions in which one of the reactants is strongly colored. The second method has apparently not been applied heretofore. It has some advantages over the photometric method: the solution can be kept in a thermostat during the experiment, shorter reaction times can be measured, and any turbidity in the solution does no harm.

For the potentiometric method, a potential between 0.6 and 0.8 volt (platinum electrode versus saturated calomel electrode) may be chosen as the reference potential. The potential 0.75 v. was chosen for the present work. The potential measured is not solely that of the Ce(IV)-Ce(III) system or of the As(V)-As(III) system, because at the beginning of the reaction it is a little greater than 0.9 v., which is not high enough to be the potential of the Ce(IV)-Ce(III) system ($E_0 = 1.40$ v. in 1 *M* sulfuric acid) nor low enough to be that of the As(V)-As(III) system ($E_0 = 0.57$ v.).

In the photometric method the transmittance of the solution was measured at 340 m$\mu$ in a spectrophotometer. The reaction time was taken as the time required for the transmittance of the solution to

increase to 40 per cent. Any value in the range 30–60 per cent transmittance could have been chosen as reference with equal precision.

An alternative way of finding the osmium concentration is to obtain the quantity of ceric cerium reduced in a given time interval, or more generally to obtain the rate of change of the ceric concentration. This involves finding the change in transmittance in a measured time interval, not necessarily from the time of mixing. This method has been used by *Lein* and *Schwartz*[3] in determining traces of iodine by catalysis of the ceric-arsenious reaction. It is particularly advantageous when the concentration of the catalyst is very low and the reaction is so slow that it would be bothersome to find the time for a given fraction of cerium(IV) to be reduced. When the reaction time is short, say less than 15 minutes, corresponding to more than $\sim 0.005\,\mu g$ Os per ml. the method described above is simpler on the whole. Reaction times as short as 30 seconds ($\sim 0.2\,\mu g$ Os per ml) can be measured to within a few per cent.

### *Factors Affecting the Reaction Rate.*

*Concentration of Osmium.* One milliliter of 0.1000 *N* ceric ammonium sulfate was added by hypodermic syringe to 4.0 ml of a mixture containing 2.00 ml of 0.1000 *N* arsenious oxide, 1.0 ml of 6 *M* sulfuric acid and various amounts of osmium as the tetroxide. The reaction times, found as already described, are given in Table II. The reciprocals of the reaction

Table II. Reaction Time at Various Osmium Concentrations (25° C).

| Osmium concentration $\mu g$ Os per ml | Reaction time | |
|---|---|---|
| | Potentiometric method min. | Photometric method min. |
| 0.200 | 0.294, 0.285 | |
| 0.160 | 0.414, 0.417 | |
| 0.120 | 0.543, 0,550 | |
| 0.100 | | 1.01, 1.00 |
| 0.080 | 0.832, 0.833 | 1.26, 1.27 |
| 0.060 | | 1.68, 1.68 |
| 0.040 | 1.79, 1.79 | 2.50, 2.52 |
| 0.020 | 3.53, 3.50 | 4.95, 4.90 |
| 0.016 | 4.37 | |
| 0.012 | 5.83 | |
| 0.010 | | 11.0, 10.7 |
| 0.008 | 8.8 | |
| 0.005 | | 20.5 |
| 0.004 | 18,5, 16,5 | |
| 0.002 | 31 | 43 |
| 0.001 | | 70 |

times for the lower osmium concentrations are plotted versus concentrations in Fig. 2. A linear relation is shown, but the best straight line (for both methods of timing) does not quite pass through the origin; it appears to intersect the $1/t$ axis at $\sim 0.002$ min$^{-1}$ or less. This behavior may be taken as evidence of a very slow reaction between ceric sulfate and

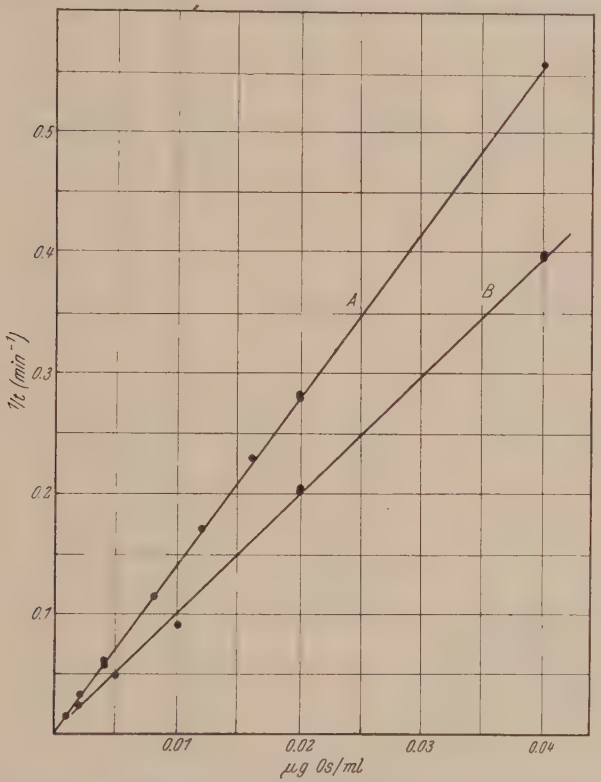


Fig. 2. Reaction Time as a Function of Osmium Concentration.
*A* potentiometric method; *B* photometric method.

arsenious acid in the absence of added osmium, and shows that for less than $\sim 0.005$ $\mu$g Os per ml account should be taken of the blank reaction. The blank is, of course, likely to vary with different batches of reagents. Some of the ceric ammonium sulfate and arsenious acid solutions used in the present work gave mixtures which were still yellow after two days.

*Temperature.* The effect of this factor, as found by the potentiometric method of measuring the rate, is shown in Fig. 3. Near 25° C, a change of 1 degree alters the reaction velocity by about 4 per cent.

*Concentration of Sulfuric Acid.* The acidity must be greater than 0.5 *M*, since otherwise the reaction does not proceed smoothly. As the

acidity is increased from 0.5 *M* to 2.5 *M* the reaction time increases and is about 2.5 times as great at the latter concentration as at the former. The action is essentially that of an electrolyte.

*Salt Effect.* For equal ionic strengths, potassium sulfate and potassium nitrate have nearly the same quantitative effect. An increase in the ionic strength of these salts from 1.5 to 3 *M* approximately doubled the reaction time. The effect of electrolytes on the rate is of no practical importance because osmium can be separated without introducing foreign electrolytes into the final solution in which it is determined.

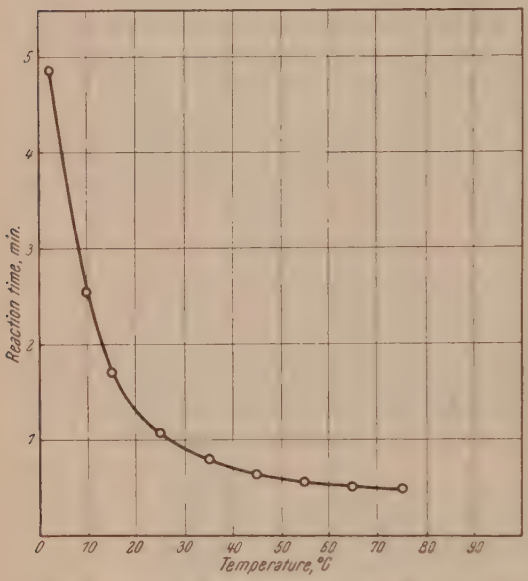


Fig. 3. Reaction Time as a Function of Temperature (0.06 μg Os per ml).

*Interfering Substances and Their Elimination.*

As already mentioned, ruthenium(VIII) and iodine (iodide) strongly catalyze the Ce(IV)-As(III) reaction. Chloride and bromide should be removed since they tend to convert osmium to quadrivalent chloro or bromo complexes such as $OsCl_6^{2-}$, which are much less catalytically active than the tetroxide. The effect of iodide, as such, can be completely eliminated by adding silver sulfate to precipitate most of it and to complex what remains in solution. Chloride, and the other halides, can be removed by evaporating the solution to fumes with sulfuric acid. A reducing agent, such as stannous tin or ferrous iron, must be added to prevent loss of osmium by oxidation to the tetroxide. In some experiments, listed in Table III, partly simulating the determination of osmium in iron meteorites, chloride and iodide were removed by adding silver ion before dissolving the iron sample in sulfuric acid.

The separation of osmium from ruthenium by extraction of osmium tetroxide with chloroform or carbon tetrachloride has been applied successfully to microgram quantities of osmium[4]. In this method the solution of osmium(VIII) and ruthenium(VIII), free from halides, is treated with a slight excess of ferrous iron to reduce both (osmium may not be completely reduced), followed by addition of nitric acid to make

its concentration about 5 *M*. This treatment leaves ruthenium in the reduced form, but oxidizes osmium to $OsO_4$, which can then be extracted by the solvents mentioned. Even when the weight ratio of ruthenium to osmium is 10000:1, a good separation is obtained. For the recovery of osmium, chloroform is slightly preferable to carbon tetrachloride as an extractant since the respective partition coefficients (organic solvent-water) are 19.1 and 13.0.

Table III. Determination of Osmium after Carbon Tetrachloride Extraction. Approximately 50 ml of aqueous solution extracted with three 10-ml portions of carbon tetrachloride, and $OsO_4$ returned to aqueous solution by shaking with 5 ml of arsenious acid-sulfuric acid.

| No.* | Addition | μg Os | |
|---|---|---|---|
| | | taken | found |
| 1 | | 0.0100 | 0.0096, 0.0094 |
| 2 | | 0.050 | 0.049, 0.048 |
| 3 | | 0.200 | 0.194, 0.196 |
| 4 | | 0.0100 | 0.0092, 0.0090 |
| 5 | 100 μg Ir(IV), 100 μg Rh(III), 100 μg Pt(IV), 100 μg Pd(II)**, 2 ml 1 *M* HCl | 0.100 | 0.096 |
| 6 | 0.5 g Fe, 3.5 mg $I^-$, 8.5 mg $Cl^-$, 100 μg Ru(III) | none | 0.0002 |
| 7 | 0.5 g Fe, 3.5 mg $I^-$, 8.5 mg $Cl^-$, 100 μg Ru(III) | 0.0100 | 0.0098, 0.0094, 0.0086, 0.0091 |
| 8 | 0.5 g Fe, 1.3 mg $I^-$, 6.6 mg $Cl^-$, 100 μg Ru(III) | 0.100 | 0.094 |
| 9 | 0.5 g Fe, 1.3 mg $I^-$, 6.6 mg $Cl^-$, 100 μg Ru(III) | 0.200 | 0.184, 0.190 |

* In Nos. 1–3, $OsO_4$ added to aqueous solution and extracted directly; in 4–9, $KMnO_4$-$Fe^{++}$-$HNO_3$ treatment applied before extraction. In 6–9 (carried out in partial simulation of determination of Os in iron meteorites), a slight excess of $Ag^+$ was added at beginning with iron metal (sulfuric acid for dissolving); silver halides later filtered off.

** Platinum metals present as chloro-complexes. Chloride removed by evaporating to fumes after addition of 10 ml 6 *M* sulfuric acid and 0.5 ml 10 per cent $SnCl_2$.

The organic solvent extract is shaken with arsenious acid-sulfuric acid solution to reduce osmium to the quadrivalent state and transfer it quantitatively to the aqueous phase. Any trace of iodine possibly carried through can be made harmless by addition of a little silver ion. The determination is finished by adding ceric sulfate to an aliquot of the arsenious acid solution and measuring the reaction time. Recoveries are usually better than 90 per cent for 0.01–0.2 μg Os in 25–50 ml of

original solution (Table III). Even with carbon tetrachloride as extractant the recovery should be about 98 per cent. Since the recoveries found are less than this, other sources of small losses evidently enter.

*Solutions.*

*Arsenious acid*, 0.100 *N*. Dissolve 4.95 g of reagent-quality $As_2O_3$ in 30 ml of 1 *M* sodium hydroxide with warming to hasten solution. Dilute to about 200 ml and make neutral or slightly acidic by adding dilute sulfuric acid (litmus paper as indicator); make up to 1 liter with water.

*Arsenious acid-sulfuric acid solution.* Dilute 500 ml of 0.10 *N* arsenious acid and 250 ml of 6 *M* sulfuric acid with water to 1 liter; 4 ml of this solution treated with 1 ml of 0.10 *N* ceric ammonium sulfate should still show a yellow color after 24 hours.

*Ceric ammonium sulfate*, 0.10 *N*. Dissolve 70 g of the dihydrate in about 250 ml of water to which 55 ml of concentrated sulfuric acid has been added. Dilute to 1 liter. Phosphate is likely to be present as an impurity in the salt and will cause a slow precipitation of ceric phosphate on standing. Therefore it is preferable to filter the solution after standing for 2 weeks.

*Osmium Tetroxide.* Prepare a stock solution by dissolving 1.0 g $OsO_4$ in 500 ml of water. Standardize this solution by *Klobbie*'s iodometric method as follows. Treat 10 ml with 15 ml of 6 *M* sulfuric acid and 2 g of potassium iodide. Titrate the liberated iodine with 0.025 *N* sodium thiosulfate, using starch as external indicator.

From this stock solution prepare more dilute solutions, e. g. 1 to 0.1 $\mu$g Os per ml, by dilution with water redistilled from alkaline permanganate. These dilute solutions should be prepared daily.

*Procedure.*

The sample solution may conveniently contain 0.025–0.5 $\mu$g Os. If halides are present, add 5 ml of 6 *M* sulfuric acid and evaporate just to fumes in the presence of a reducing agent such as ferrous sulfate. Take up the residue in about 20 ml of water and warm if necessary to bring all solid into solution.

To the cold solution add 2 or 3 ml of 85 per cent phosphoric acid and then dropwise a 5 per cent solution of potassium permanganate until a pink color appears. Discharge the permanganate color with 25 mg of ferrous ammonium sulfate; if the color is not completely discharged add another 25 mg portion. The solution should be free of any turbidity or insoluble material (e. g. higher oxides of manganese) at this point. Keep the solution cold in these operations.

Transfer the solution to a separatory funnel and add enough concentrated nitric acid to make its concentration 5–6 *M*. If necessary, cool the solution to 20–25° C and then shake vigorously for 2 minutes with 10 ml of reagent grade chloroform or carbon tetrachloride. Allow the phases to separate and run the organic solvent into another separatory funnel. Repeat the extraction of the aqueous phase with two 10-ml portions of chloroform or carbon tetrachloride; this should be sufficient for most purposes if the volume of the aqueous phase does not exceed 50 ml. Shake the combined organic solvent extracts with a few milliliters of 2 *M* nitric acid; separate the phases, shake the nitric acid solution with an equal volume of organic solvent and combine this with the main extract.

Transfer the extract to a dry glass-stoppered bottle and add exactly 5 ml of arsenious acid-sulfuric acid solution. Shake vigorously for 10 minutes (conveniently mechanically) to transfer osmium to the aqueous phase. Separate the phases carefully and add 1 mg of silver sulfate to the water solution to inactivate any trace of iodine that may be present at this point. Take a 4.00-ml aliquot of the solution (it should not be appreciably turbid) and proceed according to a) or b) below depending on whether the photometric or potentiometric technique of finding the reaction time is to be applied.

a) *Photometric.* Transfer the aliquot to a dry 10-ml beaker and, preferably while the solution is being stirred mechanically, add all at once (e. g., from a hypodermic syringe), 1.00 ml of ceric ammonium sulfate solution. For convenient timing make the addition as the hand of a stop watch crosses the 60 second mark. Transfer the solution to a dry 1-cm absorption cell and determine the time when the transmittance at 340 m$\mu$ equals 40.0 per cent. (If a filter photometer with a blue filter is used, a higher reference transmittance may have to be chosen.) Obtain the concentration of osmium by reference to a standard curve which has been established under the same conditions. Because of the large temperature coefficient, the temperature must be maintained constant to $\pm 1°$ C if the error is not to exceed $\sim 5$ per cent.

It is advisable to test beakers and cells for the possible presence of contaminating osmium by filling them with a mixture of ceric ammonium sulfate and arsenious acid-sulfuric acid solution and noting whether the yellow color will remain for a day. Vessels should be treated with ceric sulfate solution and carefully washed after use.

b) *Potentiometric.* Transfer the aliquot to a dry 10-ml beaker or other suitable vessel in a thermostat and insert a platinum wire electrode and a potassium nitrate salt bridge leading to a saturated calomel cell. While the solution is stirred mechanically, add exactly 1 ml of ceric ammonium sulfate solution at zero time. Continue the stirring and

record the time when the potential of the platinum electrode versus the calomel electrode reaches 0.75 volt or a similar arbitrary value. Establish the standard curve under the same conditions.


## Summary.

The osmium catalysis of the Ce(IV)-As(III) reaction is made the basis of a general method for the determination of 0.001 to 0.2 $\mu$g Os per milliliter. The rate of reaction can be determined photometrically or potentiometrically.

Osmium is isolated by extraction of the tetroxide with chloroform or carbon tetrachloride, and returned to aqueous medium by shaking with arsenious acid-sulfuric acid solution which is then treated with ceric ammonium sulfate to effect the final determination. Ruthenium which is also a strong positive catalyst for the Ce(IV)-As(III) reaction will be kept in reduced form and will not be extracted by the organic solvents if the solution of Os(VIII) and Ru(VIII) is treated with a slight excess of ferrous iron and then with nitric acid to make its concentration about 5 *M*. Iodine, the other strong catalyst for the reaction, can be inactivated by silver ion. Osmium recoveries of 90 per cent or better can be obtained from solutions containing as little as 0.0002 p. p. m. Os.

The kinetics of the osmium catalyzed ceric-arsenious reaction has been investigated. The rate is independent of the Ce(IV) concentration but is a function of the As(III) concentration. The slow step in the catalyzed reaction is therefore the reduction of Os(VIII) by As(III).

## Zusammenfassung.

Die Katalyse der Reaktion zwischen Ce(IV) und As(III) durch Osmium dient als Grundlage der Bestimmung des letzteren in Lösungen, die 0,001 bis 0,2 $\mu$g Osmium im Milliliter enthalten. Die Reaktionsgeschwindigkeit kann photometrisch oder potentiometrisch bestimmt werden.

Das Osmium wird als Tetroxyd mit Chloroform oder Tetrachlorkohlenstoff extrahiert. Beim Schütteln dieses Extraktes mit schwefelsaurer Lösung von arseniger Säure geht Osmiumtetroxyd in die wässerige Phase über und wird zum Zweck der quantitativen Bestimmung mit Ceriammoniumsulfat behandelt. Ruthenium, das die Reaktion beeinflußt, wird in der ursprünglichen Lösung zurückgehalten, indem man diese vor Extraktion mit dem organischen Lösungsmittel mit Ferroammoniumsulfat und Salpetersäure behandelt. Jodid, das ebenfalls die Reaktion stark beschleunigt, wird durch Zugabe von Silbersulfat unschädlich gemacht. Aus $2:10^{10}$ verdünnten Lösungen kann auf diese Weise das Osmium zu 90% und mehr wiedergefunden werden.

Die Kinetik der katalysierten Reaktion wurde untersucht. Die Reaktionsgeschwindigkeit ist eine Funktion der As(III)-Konzentration und unabhängig von der Ce(IV)-Konzentration. Die langsame Teilreaktion ist daher die Reduktion von Os(VIII) durch As(III).

**Résumé.**

La catalyse par l'osmium de la réaction Ce(IV)-As(III) est à la base d'une méthode générale pour le dosage de 0,001 à 0,2 $\mu$g d'osmium par ml. La vitesse de réaction peut être déterminée photométriquement ou potentiométriquement. L'osmium est isolé en extrayant le tétroxyde par le chloroforme ou le tétrachlorure de carbone et remis en milieu aqueux par agitation avec la solution acide arsénieux-acide sulfurique qui est alors traitée par le sulfate cérique ammoniacal pour produire le dosage final. Le ruthénium qui est aussi un catalyseur fortement positif pour la réaction Ce(IV)-As(III) sera maintenu sous la forme réduite et ne sera pas extrait par les dissolvants organiques si la solution Os(VIII) et Ru(VIII) est traitée par un léger excès de fer ferreux puis avec l'acide nitrique pour rendre sa concentration environ 5 M. L'iode, autre catalyseur positif puissant pour la réaction peut être rendu inactif par l'ion argent. A partir de solutions ne contenant que 0,0002 p. p. m. d'osmium on peut en récupérer mieux que 90%.

La cinétique de la réaction cérium-arsenic catalysée par l'osmium a été soumise à l'expérience. La vitesse est indépendante de la concentration en Ce(IV) mais c'est une fonction de la concentration en As(III). Le palier lent de la réaction catalysée est par conséquent la réduction de Os(VIII) par As(III).

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# Photometric Determination of Arsenic in Silicate Rocks.

By

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With 1 Figure.

*(Received February 10, 1953.)*

For many of the heavy metals occurring as traces in silicate rocks, modern colorimetric methods are equal if not superior to spectrographic methods in sensitivity and accuracy. The spectrographic determination of arsenic is of low sensitivity (0.01% $As_2O_5$)[1] and there is thus special need of a colorimetric method for its determination in silicate rocks, in which the content usually falls in the range 0.5–10 p. p. m. Arsenic can be determined very sensitively by neutron activation (procedures have been described for sea water[2] and biological materials[3]), but this method need not be resorted to for the amounts of arsenic that are normally present in rocks.

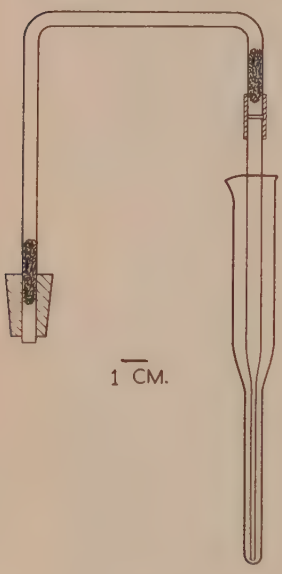


Fig. 1. Apparatus for Absorption of Arsine.

The following method involves fusion of the silicate sample with sodium hydroxide or sodium hydroxide-peroxide, evolution of arsenic as arsine from the filtered leach of the melt, and final determination as molybdenum blue.

## *Apparatus.*

A 50-ml Erlenmeyer flask serves for the evolution of arsine. The absorption tube is shown in Fig. 1. Two plugs of glass wool are inserted in the delivery tube to prevent entrained droplets of solution from being carried with the gas into the absorbing solution. The first plug should be replaced daily. Since

* Fulbright Scholar.

phosphate reacts in the same way as arsenic in the final color development, it is important to prevent any of the sample solution from finding its way into the absorbing solution. The second plug, on the right hand side, may be soaked in lead acetate solution and dried, to absorb any hydrogen sulfide that may be evolved.

### *Solutions.*

*Stannous chloride*, 40 g of the dihydrate in 100 ml of concentrated hydrochloric acid. Prepare fresh monthly.

*Potassium iodide*, 15 g in 100 ml of water.

*Iodine-potassium iodide.* Dissolve 0.25 g of iodine in a small volume of water containing 0.4 g of potassium iodide and make up to 100 ml.

*Sodium bicarbonate*, 0.5 *M*, 4.2 g in 100 ml of water.

*Sodium metabisulfite*, 0.5 g in 10 ml of water. Prepare fresh daily.

*Ammonium molybdate-hydrazine sulfate.* Prepare immediately before use by mixing 10.0 ml each of solutions *A* and *B* and diluting to 100 ml with water. *Solution A:* dissolve 1.0 g of ammonium molybdate in 10 ml of water and add 90 ml of 6 *N* sulfuric acid. *Solution B:* dissolve 0.15 g of hydrazine sulfate in 100 ml of water.

*Standard arsenic solution.* Dissolve 0.132 g of pure $As_2O_3$ in 2 ml of 1 *N* sodium hydroxide, dilute with water, make slightly acidic with hydrochloric acid, and dilute to 100 ml with water. From this stock solution (1.00 mg As per ml) prepare a standard solution containing 0.010 mg of As per ml by diluting with water.

### *Procedure.*

Fuse 2.5 g of reagent-quality sodium hydroxide in a nickel crucible. After cooling add 0.50 g of 100-mesh rock powder and 0.25 g of sodium peroxide (the use of the latter is not strictly necessary). Cautiously heat to fusion (the initial reaction may be vigorous) and keep at dull redness for 20 to 30 minutes or until it is judged that decomposition is complete. Cool, add 8 ml of water, and heat on a steam bath to disintegrate the melt. Filter through a small paper of medium texture and wash ten times with small portions (1 to 2 ml) of water or 0.1% sodium hydroxide. Catch the filtrate and washings in a 50-ml Erlenmeyer flask. The volume at this point should not exceed 25 ml.

Cool the solution and add 11 ml of hydrochloric acid dropwise with swirling. Disregard any separation of silica. Then add 2 ml of potassium iodide solution and 1.0 ml of stannous chloride solution. Allow the mixture to stand at room temperature for 15 to 30 minutes or heat to 80 to 90° C for 5 minutes and then cool to room temperature.

Measure 1.0 ml of iodine-potassium iodide solution and 0.2 ml of sodium bicarbonate solution into the absorption tube. Mix with the end of the delivery tube. Quickly add 2.0 g of 20- to 30-mesh zinc (reagent quality, "arsenic-free"), to the evolution flask, immediately insert the stopper, and allow the gases to bubble through the absorbing solution for 30 minutes without heating the flask. At the end of this time the solution should still contain some iodine. Disconnect the delivery tube and leave it in the absorption tube. Add 5.0 ml of ammonium molybdate-hydrazine sulfate reagent, a drop of sodium metabisulfite solution, and mix well (the color of iodine should disappear). Heat for 15 minutes in a water bath at 95 to 100° C, cool, transfer the solution to a 10-ml volumetric flask, and dilute to the mark with water.

Obtain the transmittance of the solution with the aid of a spectrophotometer or filter photometer at 840 m$\mu$ or with a red filter showing maximum transmission above 700 m$\mu$. Measure against a blank solution obtained as follows. Mix 1.0 ml of iodine-potassium iodide solution, 0.2 ml of sodium bicarbonate solution, 5.0 ml of ammonium molybdate-hydrazine sulfate reagent, and a drop of sodium metabisulfite. Heat for 15 minutes in a water bath at 95 to 100°, cool, and make up to 10 ml.

Construct the standard curve by taking various amounts of arsenic (e. g. 2.5, 5.0 and 7.5 $\mu$g), mixing with 1 ml of iodine-iodide solution and 0.2 ml of sodium bicarbonate solution, then adding 5 ml of molybdate-hydrazine sulfate reagent and a drop of bisulfite, heating, diluting to 10 ml and determining the transmittance. A plot of $\log I_0/I$ versus concentration of arsenic should give a straight line.

Take a blank through the whole procedure and deduct any arsenic found from the sample value. Make certain also that the apparatus used provides complete absorption of arsenic by testing it with a known amount.

## Discussion.

Tables I and II contain the results obtained by applying the proposed method to a quartz monzonite and a diabase to which known amounts of arsenic (as sodium arsenite) were added. Results are shown for both sodium hydroxide and sodium hydroxide-peroxide fusion. For the two rocks tested, the two methods of decomposition give equally good recoveries. A mixture of sodium hydroxide and sodium peroxide is an excellent flux for decomposition of sulfides[4]. As far as the determination of small amounts of arsenic is concerned, however, sodium hydroxide alone (cf. *Wilson*[5]) appears to be satisfactory as shown by results obtained with pyrite. A sample of pyrite (Leadville, Colorado), brought into solution with nitric and hydrochloric acids and the arsenic photometrically determined after distillation of the chloride, gave 0.0137% As. Photo-

metric determination after sodium hydroxide fusion gave 0.0135% As, and after sodium hydroxide-peroxide fusion 0.0131% As. Addition of sodium peroxide gives a more fluid melt than sodium hydroxide alone.

Table I. Determination of Arsenic in a Quartz Monzonite* after Sodium Hydroxide and Sodium Hydroxide-Peroxide Fusion.

| NaOH Fusion | | | $NaOH-Na_2O_2$ Fusion | |
|---|---|---|---|---|
| As taken p. p. m. | As found | | As taken p. p. m. | As found in filtrate p. p. m. |
| | in filtrate p. p. m. | in residue p. p. m. | | |
| 0.0 | 0.0, 0.0 | 0.0, 0.0 | 0.0 | 0.0 |
| 0.5 | 0.6 | | 0.5 | 0.6 |
| 1.0 | 1.2 | | 1.0 | 1.2 |
| 2.2 | 2.2, 2.2 | 0.0, 0.0 | 2.2 | 2.2, 2.4 |
| 4.4 | 4.4, 4.2 | 0.0, 0.0 | 4.4 | 4.4, 4.6 |
| 9.0 | 9.2, 9.0 | | 9.0 | 9.0 |
| 11.2 | 11.2 | | 11.2 | 11.2 |
| 13.4 | 13.4, 12.6 | | 13.4 | 12.8, 13.4 |
| 20.0 | 19.8, 19.4 | 0.4, 0.0 | 20.0 | 19.0, 19.0 |

* Original As content of quartz monzonite = 0.0 p. p. m., an unusually low value.

Table II. Determination of Arsenic in Diabase* after Sodium Hydroxide and Sodium Hydroxide-Peroxide Fusion.

| NaOH Fusion | | | $NaOH + Na_2O_2$ Fusion | | |
|---|---|---|---|---|---|
| As taken** p. p. m. | As found | | As taken** p. p. m. | As found | |
| | in filtrate p. p. m. | in residue p. p. m. | | in filtrate p. p. m. | in residue p. p. m. |
| 1.4 | 1.4 | | 1.4 | 1.2 | 0.0 |
| 2.4 | 2.4 | | 2.4 | 2.4 | |
| 3.6 | 3.6, 3.6 | | | | |
| 5.8 | 5.6, 5.8 | 0.0 | 5.8 | 5.8 | 0.2 |
| 10.4 | 10.0, 10.4 | 0.0 (0.8) | | | |
| 12.6 | 12.4 | 0.0 | 11.4 | 11.0 | |
| 14.8 | 14.6 | 0.0 | | | |
| 21.4 | 20.0, 20.2, 20.0 | 0.2 | 21.4 | 21.6 | 0.4 |

* Percentage composition: 52.7 $SiO_2$, 15.0 $Al_2O_3$, 7.4 $Fe_2O_3$, 5.6 FeO, 3.7 MgO, 8.0 CaO, 3.2 $Na_2O$, 1.1 $K_2O$, 1.8 $TiO_2$, 0.25 $P_2O_5$, 0.24 MnO, 0.02 S.
** Includes original As in diabase, 1.4 p. p. m.

The amount of arsenic retained in the washed residue is small enough to be neglected. Recovery of added arsenic is usually better than 95% for the range investigated. The method appears to be accurate enough to satisfy present day requirements.

Arsenic can be determined with fair accuracy without filtration of the leached melt if modifications are introduced to provide for the effect of iron (Table III). In the presence of iron, evolution of hydrogen is more rapid than in its absence and therefore two absorption tubes in series should be used; moreover, more stannous chloride must be added, since otherwise the evolution of arsine is incomplete. Since two absorbing solutions are used, and the final volume is doubled, sensitivity and precision are adversely affected. Filtration is generally recommended.

Table III. Determination of Arsenic without Filtration after Sodium Hydroxide Fusion.

| Sample | As taken p. p. m. | As found p. p. m. |
|---|---|---|
| Quartz monzonite | 2.2 | 2.2 |
| ,, ,, | 4.4 | 4.4, 4.0 |
| ,, ,, | 9.0 | 8.2 |
| ,, ,, | 13.4 | 12.2 |
| ,, ,, | 20.0 | 18.2, 18.6 |
| Diabase | 1.4 | 1.0 |
| ,, | 5.8 | 2.8 |
| ,, | 10.4 | 6.4 |
| ,, | 10.4 | 7.6* |
| ,, | 10.4 | 10.4** |
| ,, | 21.4 | 10.0 |
| ,, | 21.4 | 20.4*** |

* 1.0 ml stannous chloride solution; 2 absorption vessels in series used, giving 7.4 + 0.2 p. p. m. As.

** 2.0 ml stannous chloride solution; 2 absorption vessels in series, giving 9.8 + 0.6 p. p. m. As.

*** 2.0 ml stannous chloride solution; 2 absorption vessels in series, giving 19.0 + 1.4 p. p. m. As.

Few, if any, elements likely to be encountered in igneous rocks will interfere in the proposed method. A number of elements were added to a sample of 0.5 g diabase, the arsenic content of which was 1.4 p. p. m., and the following values were obtained: 1.2 p. p. m. As in presence of 1 mg Cu and 1 mg Ag; 1.4 p. p. m. As with 1 mg $GeO_2$; 1.4 p. p. m. As with 1 mg $TeO_2$; 1.4 p. p. m. As with 5 mg $WO_3$ and 5 mg $V_2O_5$; and 1.4 p. p. m. As with 10 mg Ni and 5 mg Co. The rate of evolution of hydrogen is increased by nickel and cobalt, and large amounts of these, if not removed by filtering off the residue from the leach of the melt, might lead to low results. Molybdenum, chromium, and antimony (10 $\mu$g) are known not to interfere[6].

Sodium carbonate and sodium carbonate-nitrate are not as satisfactory fluxes as sodium hydroxide or sodium hydroxide-peroxide (Table IV).

Table IV. Determination of Arsenic after Sodium Carbonate and Sodium Carbonate-Nitrate Fusion. Arsenic determined in the filtrate of the leached melt.

| Sample | $Na_2CO_3$ | | $Na_2CO_3 + NaNO_3$ | |
|---|---|---|---|---|
| | As taken p. p. m. | As found p. p. m. | As taken p. p. m. | As found p. p. m. |
| Quartz monzonite | 2.2 | 1.8 | | |
| Diabase | 1.4 | 1.0 | 1.4 | 1.4 |
| Diabase | 10.4 | 9.0, 8.0* | 10.4 | 8.8, 9.2** |
| Gabbro | 3.6 | 2.6 | 3.6 | 3.6 |

* As in washed residue = 0.8 p. p. m.
** As in washed residue = 0.8 p. p. m.

Standard procedures are followed for the evolution and absorption of arsine and for the photometric determination of arsenic. A solution of iodine in potassium iodide and sodium carbonate, as recommended by *Milton* and *Duffield*[7], is used as the absorbing solution for arsine and appears to be as effective as the mercuric chloride-potassium permanganate mixture used by one of the authors in an earlier procedure; it has the advantage of not requiring subsequent filtration for removal of mercurous chloride. Hydrazine sulfate is preferred to stannous chloride for the reduction of molybdiarsenate, since it gives more reproducible results. At least for small quantities of arsenic, corresponding to a few parts per million of sample, the limiting factor in the accuracy appears to be the photometric error. In the present work a Leitz-Rouy photometer with a 640 m$\mu$ filter was used. With a 1-cm cell this gave a $\log I_0/I$ of 0.1 for 1 $\mu$g As per milliliter of solution. With a final volume of 10 ml, an error of 0.001 in $\log I_0/I$ results in an error of 0.2 p. p. m. of As in the sample (0.5 g). By making replicate transmittance readings, the photometric error can be kept below this value. The sensitivity, and therewith the accuracy for small amounts of arsenic, can be increased by using a spectrophotometer instead of a filter photometer and measuring the transmittance at about 840 m$\mu$, or by using a path length greater than 1 cm.

The reagents used in the present work contained no detectable arsenic, i. e., less than 0.1 p. p. m. As on the basis of 0.5 g rock sample.

## Summary.

The method described consists in decomposing the silicate rock sample by fusion with sodium hydroxide or sodium hydroxide-peroxide, leaching the melt with water, evolving arsine from the filtrate, and finally determining arsenic by photometric evaluation of molybdenum blue. Satisfactory accuracy has been demonstrated for the range 0.0 to 20 p. p. m. As, for which the method is particularly intended.

**Zusammenfassung.**

Zur Bestimmung des Arsengehaltes in Silikatgesteinen wird die Probe durch Schmelzen mit Natriumhydroxyd und gegebenenfalls Natriumperoxyd aufgeschlossen. Aus dem Filtrat der wäßrigen Lösung dieser Schmelze wird Arsenwasserstoff entwickelt und in natriumhydrogenkarbonathältiger Jodlösung aufgefangen. Das hierbei entstehende Arsenat wird nach Zugabe von Molybdatreagens und Bisulfit photometrisch bestimmt. Für Arsengehalte unter 0,02 $^0/_{00}$ werden nach dieser Methode Resultate von zufriedenstellender Genauigkeit erhalten.

**Résumé.**

La méthode décrite consiste en la décomposition de l'échantillon de roche silicatée par fusion avec la soude ou le peroxyde de sodium, reprenant la partie fondue par l'eau, libérant l'hydrogène arsénié du filtrat et finalement dosant l'arsenic par colorimétrie du bleu de molybdène. Une précision suffisante a été mise en évidence dans le domaine de 0,0 à 20 p. p. m. d'arsenic pour lequel la méthode convient particulièrement bien.

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# Absorption Train for Determination of Carbon and Hydrogen.

By

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With 1 Figure.

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A critical part of the apparatus in the determination of carbon and hydrogen by dry combustion is the connection between the combustion tube and the absorption tubes. Rubber connections are most frequently used, but they have the disadvantage of allowing large amounts of carbon dioxide and water to diffuse through their walls[1]. Unlubricated glass joints are frequently used[2–5]. It is, however, difficult to obtain a tight connection with these joints and the risk of breakage is considerable. The present author has used lubricated joints, avoiding the risk of breakage by the use of ball and socket joint links[6]. This method gives good results but has the disadvantage of requiring a somewhat delicate cleaning procedure for the lubricated joints.

Some years ago E. I. Du Pont De Nemours & Co. Inc. marketed the plastic material "Teflon" (polytetrafluoroethylene) which has some very outstanding qualities. According to the Plastics Encyclopedia[7] the water absorption of Teflon of $^1/_8$ inch thickness is 0.00% in 24 hours; and concerning carbon dioxide the Technical Service of Du Pont De Nemours says: "... the permeability rate of 'Teflon' to carbon dioxide gas is $99.2 \cdot 10^{-15}$ moles/cm²/sec/cm Hg of partial pressure differential for 1 cm thickness. These results were obtained on a sample of 'Teflon' film produced by an extrusion process. The sample was 0.005" thick, and had been conditioned at 23° C and 50% relative humidity for 40 hours prior to testing. If the sample and the carbon dioxide gas were both perfectly dry, it is anticipated that the permeability rate might be as little as a third of the given value."[8]

Links for the absorption train[6] were made of "Teflon" as shown in Fig. 1. The tapered glass joints of the absorption tubes were polished

with moist ferric oxide. "Teflon" tube *D* is cemented to the side tube *E* of the scrubber with polyethylene. The side tubes of the scrubber were treated with a silicone reagent in order to avoid the adsorption of water from the air. The scrubber is filled with manganese dioxide[9]. The ball and socket joints are lubricated with silicone grease.

From the figures given above it can be calculated that a loss of $10^{-5}$ to $10^{-4}$ mg of carbon dioxide caused by diffusion can be expected if the partial pressure of carbon dioxide in the combustion gases is assumed to be 1.5 cm Hg, the contact surface between the gas and the "Teflon"

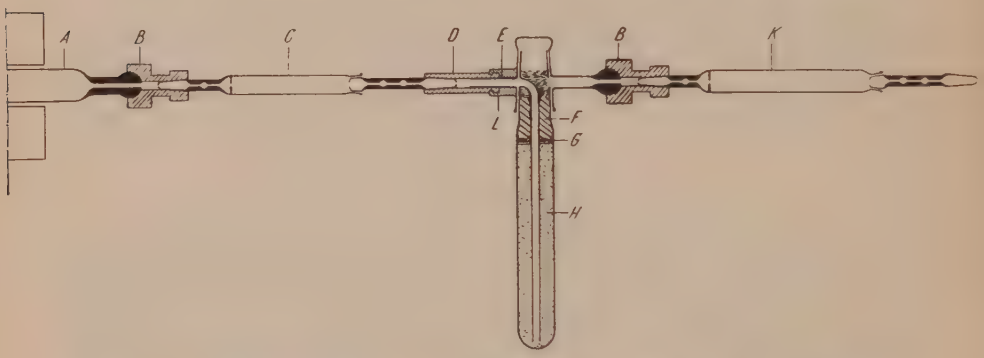


Figure 1. *A* = combustion tube, *B* = socket joint-tapered joint links made of "Teflon" and held together with the ball joints by means of clamps, *C* = water absorption tube, *D* = tapered joint link made of "Teflon" and cemented to the side tube *E* of the scrubber with polyethylene, *F* = magnesium perchlorate, *G* = pyrex wool, *H* = manganese dioxide, *K* = carbon dioxide absorption tube, *L* = polyethylene.

about 1 cm², the thickness of the "Teflon" wall about 3 mm, and the time of contact 20 minutes. No losses could be substantiated in actual analyses.

As the "Teflon" is slightly elastic the tapered joints hold tightly to the polished glass joints and no lubrication is necessary. This makes it possible to remove the absorption tubes from the combustion tube and to weigh them without previous wiping or other cleaning, which makes the work much easier for the analyst and shortens the time necessary for conditioning the absorption tubes before the weighing.

The author is very indebted to *Einar Stenhagen* for his interest in the work, to E. I. Du Pont De Nemours & Co., Inc., for valuable information and to *Endel Sepp* for drawing the figure. The apparatus is available from Nicroma, Klara Västra Kyrkogata 7, Stockholm.

## Summary.

The use of "Teflon" joint links between combustion tube and absorption tubes gives a tight connection without lubrication and obviates the need of wiping or other cleaning of the tubes between the analyses.

**Zusammenfassung.**

Schliffverbindungen aus Teflon zwischen dem C-H-Verbrennungsrohr und den Absorptionsröhrchen geben ohne Fetten eine dichte Verbindung und machen es möglich, die Röhrchen zwischen den Analysen ohne vorheriges Abwischen oder anderweitiges Reinigen direkt zu wägen.

**Résumé.**

L'emploi de joints de «Teflon» entre le tube à combustion et les tubes à absorption donne une connexion hermétique sans graissage et évite la nécessité d'essuyer et de nettoyer les tubes entre les analyses.

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# Beiträge zur Methylimidbestimmung.

2. Mitteilung:

## Das Verhalten von Äthyljodid gegenüber Natriumthiosulfat und anderen Waschflüssigkeiten; gleichzeitig ein Beitrag zur Unterscheidung von Methyl- und Äthylgruppen.

Von

**Fr. Franzen, W. Disse und K. Eysell.**

*(Eingelangt am 2. März 1953.)*

In unserer 1. Mitteilung[1] wurde analytisch belegt, daß sich das in der neueren und neuesten Literatur[2–14] als Waschflüssigkeit angegebene Natriumthiosulfat mit Methyljodid, dem Reaktionsprodukt der Methylimid- und Methoxyl-Bestimmung, umsetzt. Das Ausmaß der Umsetzung erwies sich abhängig von Konzentration, Menge und Temperatur der vorgelegten Natriumthiosulfatlösung sowie von der gleichzeitigen Anwesenheit bzw. Konzentration bestimmter ionisierter Verbindungen (z. B. Natriumchlorid, Cadmiumsulfat). Die dadurch bedingten Analysendefizite (s. 1. Mitt.[1], Tabelle 1) betragen z. B. bei Verwendung von 4 ml 5%iger Natriumthiosulfat-Waschflüssigkeit 36% Methyljodid.

Es lag nun nahe festzustellen, ob und in welchem Ausmaß sich Äthyljodid, das Reaktionsprodukt der Äthylimid- und Äthoxyl-Bestimmung, mit wassergelöstem Natriumthiosulfat umsetzt. Gleichzeitig wurden auch die übrigen in der Literatur angegebenen Waschflüssigkeiten auf diese Frage hin geprüft. Die diesbezüglichen Untersuchungsergebnisse sind in Tabelle 1 zusammengefaßt. Aus Vergleichsgründen wird der entsprechende Prozentsatz der Umsetzung mit Methyljodid in einer Nebenspalte angeführt.

Die Einwaage des flüchtigen Äthyljodids in kleinen, dünnwandigen Phiolen (Technik s. 1. Mitt.[1], Fußnote auf S. 279) erfolgte auf der Mikrowaage. Die Versuchsanordnung war im übrigen der in unserer 1. Mitt. angegebenen völlig gleich.

Wie aus Tabelle 1 hervorgeht, setzt sich wassergelöstes Natriumthiosulfat auch mit Äthyljodid um. Im Vergleich zum Methyljodid ist das Ausmaß der Umsetzung geringer; während z. B. 4 ml einer 5%igen Natriumthiosulfatlösung unter den für die Alkoxyl- und Alkylimidbestimmung gegebenen Bedingungen 36% des im $CO_2$-Strom durchtretenden Methyljodids durch chemische Umsetzung binden, beträgt das Analysendefizit für Äthyljodid 8%. Für andere Thiosulfatkonzentrationen bzw. -kombinationen ergeben sich entsprechende Verhältnisse (s. Tabelle 1). Lediglich die Kombination 10%iges Natriumthiosulfat + 10%iges Cadmiumsulfat zeigt keinerlei Umsetzung mit dem im Kohlendioxydstrom durchtretenden Äthyljodid.

Die Tatsache der Umsetzung zwischen wassergelöstem Natriumthiosulfat und Methyl- bzw. Äthyljodid wurde bereits — wenn auch in anderem Zusammenhang und unter anderen Bedingungen — in den Jahren 1874 bis 1904 von *Bunte*[23], *Spring* und *Legros*[24] sowie *Slator*[25] festgestellt.

Auf Grund vorstehender Untersuchungen muß gesagt werden, daß sich wassergelöstes Natriumthiosulfat nicht als Waschflüssigkeit für die Äthylimid- und Äthoxylbestimmung eignet, da es einen nennenswerten Minusfehler im Analysenergebnis verursachen würde. Alle übrigen Waschflüssigkeiten, insbesondere wassergelöstes Natriumantimonyltartrat (10%ig)[21], Hydroxylaminchlorhydrat (5%ig, mit Natriumcarbonat alkalisiert)[21], Hydrazin (5%ig)[1], Ascorbinsäure (5%ig)[22] oder Phosphorsuspension[17–20] dürfen als voll geeignet verwendet werden. Die Notwendigkeit der Zwischenschaltung einer Waschflüssigkeit wurde in der 1. Mitt.[1] begründet.

Mit unserer Feststellung, daß sich wassergelöstes Natriumthiosulfat unter den Bedingungen der Alkylimid- und Alkoxyl-Bestimmung auch mit Äthyljodid umsetzt, konnten wir *Whites*[12] Untersuchungen nicht bestätigen, der wohl für Methyljodid, nicht aber für Äthyljodid eine solche Reaktion beobachtete.

In seiner diesbezüglichen Mitteilung berichtet *White*[12], mit reinem Methyljodid gearbeitet zu haben; leider sind hierfür keine Beleganalysen mit genauer Arbeitsangabe aufgeführt. Ob *White* auch mit reinem Äthyljodid gearbeitet hat, geht aus seiner Veröffentlichung nicht hervor. An Beleganalysen führt er lediglich Substanz-Bestimmungen an einer methoxyl- und einer äthoxylhaltigen Verbindung auf. Nun fragt es sich, inwieweit der zur Diskussion stehende Sachverhalt an Substanzbestimmungen mit Sicherheit beurteilt werden kann. Hierbei ist die Gefahr sehr groß, daß ein eventuelles Analysendefizit durch einen hohen Analysenblindwert — vor allem bei Verwenden einer zu geringen Menge Waschflüssigkeit — kompensiert bzw. verschleiert wird.

*White* verwendete bei seinen Analysen nur 0,5 bzw. 1,0 ml Waschflüssigkeit. Hierbei wird das Ausmaß der Umsetzung zwischen wassergelöstem Natriumthiosulfat und Äthyljodid natürlich geringer, als wenn man, wie wir es aus

Tabelle I. Das Verhalten einer Reihe von für die Alkoxyl- und Alkylimidbestimmung angegebenen Waschflüssigkeiten in Bezug auf den quantitativen Durchtritt von Äthyljodid (vergleichsweise auch von Methyljodid).

| Waschflüssigkeit | | $C_2H_5J$-Durchtritt | | | | $CH_3J$-Durchtritt[1] |
|---|---|---|---|---|---|---|
| Art und Konzentration | Menge ml | Einwaage mg | Gefunden mg | Gefunden % | Mittel % | Mittel % |
| Aqua bidest. (ohne Nachperlen) | 4 | 1,601 | 1,598 | 99,87 | | |
| | | 2,030 | 2,026 | 99,85 | 99,87 | 99,83 |
| | | 2,619 | 2,616 | 99,88 | | |
| Aqua bidest. (mit Nachperlen) | 4 | 1,792 | 1,794 | 100,11 | | |
| | | 1,689 | 1,691 | 100,10 | 100,03 | 100,0 |
| | | 3,347 | 3,342 | 99,87 | | |
| 5% $Na_2S_2O_3$[6] | 4 | 1,420 | 1,305 | 91,90 | | |
| | | 2,050 | 1,888 | 92,09 | 91,99 | 63,15 |
| | | 1,962 | 1,805 | 91,99 | | |
| 5% $Na_2S_2O_3$[12] | 1 | 1,855 | 1,807 | 97,41 | | |
| | | 1,507 | 1,465 | 97,21 | 97,31 | 84,08 |
| | | 2,775 | 2,699 | 97,25 | | |
| | | 2,118 | 2,061 | 97,38 | | |
| 5% $Na_2S_2O_3$[6,14] + 0,5% $Na_2CO_3$ | 4 | 1,929 | 1,772 | 91,98 | | |
| | | 2,110 | 1,946 | 92,23 | 92,04 | 63,77 |
| | | 1,421 | 1,306 | 91,90 | | |
| 1,5% $Na_2S_2O_3$[5] + 0,5% $Na_2CO_3$ | 4 | 2,340 | 2,306 | 98,55 | | |
| | | 3,490 | 3,425 | 98,15 | 98,27 | 76,45 |
| | | 4,390 | 4,307 | 98,10 | | |
| 40% $Na_2S_2O_3$ | 4 | 1,585 | 1,500 | 94,63 | | |
| | | 2,608 | 2,470 | 94,70 | 94,63 | |
| | | 1,769 | 1,673 | 94,57 | | |
| 40% $Na_2S_2O_3$[12] | 1 | 2,775 | 2,709 | 97,63 | | |
| | | 2,700 | 2,647 | 98,86 | 98,63 | 93,72 |
| | | 4,340 | 4,301 | 99,09 | | |
| | | 2,822 | 2,783 | 98,96 | | |
| 10% $Na_2S_2O_3$ + 10% $CdSO_4$[8] | 4 | 2,235 | 2,231 | 99,82 | | |
| | | 1,600 | 1,598 | 99,87 | 99,89 | 96,02 |
| | | 2,968 | 2,963 | 99,83 | | |
| | | 2,338 | 2,349 | 100,04 | | |
| 5% $Na_2S_2O_3$ in gesättigter NaCl-Lösung | 4 | 2,657 | 2,630 | 98,98 | | |
| | | 1,832 | 1,812 | 98,90 | 98,99 | 96,32 |
| | | 2,004 | 1,986 | 99,10 | | |

*(Fortsetzung der Tabelle 1.)*

| Waschflüssigkeit | | $C_2H_5J$-Durchtritt | | | | $CH_3J$-Durchtritt[1] |
|---|---|---|---|---|---|---|
| Art und Konzentration | Menge ml | Einwaage mg | Gefunden mg | Gefunden % | Mittel % | Mittel % |
| 5% $Na_2S_2O_3$ in gesättigter NaCl-Lösung[12] | 1 | 2,729 | 2,731 | 100,07 | | |
| | | 2,735 | 2,731 | 99,84 | 99,97 | **99,56** |
| | | 2,614 | 2,622 | 100,30 | | |
| | | 3,400 | 3,389 | 99,67 | | |
| 5% $CdSO_4$[15,16] | 4 | 2,007 | 2,004 | 99,83 | 99,95 | 100,02 |
| | | 2,172 | 2,174 | 100,08 | | |
| 5% $Na_2CO_3$ | 4 | 2,394 | 2,384 | 99,59 | 100,06 | 99,99 |
| | | 3,458 | 3,477 | 100,54 | | |
| Phosphor in Aqua bidest.[17–20] | 4 | 2,474 | 2,470 | 99,83 | 100,08 | 100,01 |
| | | 2,410 | 2,418 | 100,33 | | |
| 10% Natriumantimonyltartrat[21] | 4 | 1,557 | 1,557 | 100,0 | | |
| | | 2,091 | 2,088 | 99,85 | 99,90 | 99,99 |
| | | 2,030 | 2,027 | 99,85 | | |
| 5% $NH_2OH \cdot HCl$ ($Na_2CO_3$)[21] | 4 | 2,434 | 2,427 | 99,72 | | |
| | | 1,900 | 1,903 | 100,15 | 100,03 | 100,01 |
| | | 2,566 | 2,572 | 100,23 | | |
| 5% 1-Ascorbinsäure[22] | 4 | 2,537 | 2,535 | 99,91 | | |
| | | 1,583 | 1,580 | 99,81 | 99,95 | 99,98 |
| | | 1,414 | 1,416 | 100,14 | | |
| 5% $NH_2$—$NH_2$[1] | 4 | 1,530 | 1,525 | 99,67 | | |
| | | 1,768 | 1,766 | 99,88 | 99,87 | 100,0 |
| | | 1,858 | 1,859 | 100,05 | | |

grundsätzlichen Erwägungen* handhaben, 4 ml Waschflüssigkeit vorlegt. Immerhin beträgt auch bei Vorlegen von nur 1 ml 5%iger Natriumthiosulfat-Waschflüssigkeit das Analysendefizit für Äthyljodid noch 2,69% (s. unsere Tabelle 1). Anderseits bedingt die von *White* verwendete geringe Waschflüssigkeitsmenge infolge unzureichender Jodwasserstoffabsorption einen größeren Analysenblindwert, was zur Kompensierung bzw. Verschleierung des tatsächlich vorliegenden Analysendefizits führt. Auf Grund dieser Wechselbeziehungen dürften die von *White* gemachten, von unseren Untersuchungsergebnissen abweichenden Angaben zu erklären sein.

* Auf Grund der in unserer 1. Mitt.[1] besprochenen Schwierigkeit, den im Kohlendioxydstrom der Alkoxyl- und Alkylimidbestimmung regelmäßig mitgeführten Jodwasserstoff vollständig zu eliminieren, halten wir die Verwendung von wenigstens 4 ml Waschflüssigkeit — am besten auf zwei Wäscher verteilt — für erforderlich. Außer von der Ionensättigung und der Destillationstechnik hängt die Größe des Analysenblindwertes vor allem von der Menge der eingefüllten Waschflüssigkeit ab.

Die Alkylimid- bzw. Alkoxylbestimmung als solche gibt keine Auskunft über die Art der in einer unbekannten Verbindung vorliegenden Alkylgruppe. Zur Entscheidung, ob das in der Vorlage ermittelte Alkyljodid einer Methyl- oder einer Äthylgruppe entstammt, ist man auf modifizierte bzw. zusätzliche Verfahren angewiesen, so auf die Methoden von *Beckmann*[26], *Willstaetter* und *Utzinger*[27], *Kuester* und *Maag*[28], *Friedrich*[29,6], *Furter*[31] oder *Kuhn* und *Roth*[30,14].

*White*[12] schlug nun vor, seine Feststellung, daß sich wassergelöstes Natriumthiosulfat nur mit Methyljodid, nicht aber mit Äthyljodid umsetzt, zur Unterscheidung der beiden Alkylgruppen auszunutzen. Dieser einfache Weg wird in der Tat gangbar, wenn man den vorstehend besprochenen Irrtum *White*s entsprechend berücksichtigt. Verwendet man in einer ersten Alkylimid- oder Alkoxylbestimmung eine Waschflüssigkeit, die sich weder mit Methyljodid noch mit Äthyljodid umsetzt, und in einer zweiten Bestimmung eine 5%ige Natriumthiosulfatlösung (4 ml)* als Waschflüssigkeit, so beweist ein um 8% niedriger liegendes Analysenergebnis das Vorliegen einer Äthylgruppe, ein um 36% differierendes dagegen das Vorhandensein einer Methylgruppe.

Hält man neben dem Tempo des Kohlendioxydstromes vor allem die Konzentration und Menge der verwendeten Waschflüssigkeiten sorgfältig gleich, so erweist sich das Ausmaß der Umsetzung des wassergelösten Natriumthiosulfats mit dem Methyl- bzw. Äthyljodid als eine absolut zuverlässige Konstante; es kann deshalb ohne Bedenken zur Unterscheidung von Methyl- und Äthylgruppen herangezogen werden. Es sei eigens darauf hingewiesen, daß bei Substanzbestimmungen auftretende Abweichungen von den konstanten Umsetzungsverhältnissen nicht auf Schwankungen dieser Umsetzung selbst zurückzuführen sind, sondern auf Plus-Minusfaktoren der Routinemethode, über deren Ursache und Behebung in einer späteren Mitteilung berichtet werden soll.

Der vorstehend kurz skizzierte Weg, die Natur des über Sauerstoff oder Stickstoff gebundenen Alkyls lediglich unter Verwendung zweier verschiedener Waschflüssigkeiten bei sonst völlig gleichem Verfahren zu klären, ist den oben aufgeführten Verfahren in zeitlicher und apparatetechnischer Hinsicht an Einfachheit überlegen; an Genauigkeit steht er diesen nicht nach.

* Es wird deshalb die 5%ige Natriumthiosulfatlösung (mit 0,5% Natriumcarbonatzusatz) vorgeschlagen, weil hierbei der mengenmäßige Unterschied in der Umsetzung des wassergelösten Natriumthiosulfats mit Methyl- bzw. Äthyljodid am stärksten in Erscheinung tritt. Das Volumen von 4 ml solcher Waschflüssigkeit wird deshalb angegeben, weil es einmal zur Eliminierung von im Kohlendioxydstrom mitgeführtem Jodwasserstoff und Jod unbedingt erforderlich ist, anderseits aber auch, wie aus Tabelle 1 hervorgeht, das Ausmaß der festzustellenden Umsetzung mitgestaltet.

## Zusammenfassung.

Unter Verwendung von in Phiolen eingewogenem, reinem Äthyljodid konnte nachgewiesen werden, daß sich wassergelöstes Natriumthiosulfat unter den Bedingungen der Alkylimid- und Alkoxylbestimmung auch mit Äthyljodid umsetzt. Das Ausmaß der Umsetzung ist im Vergleich zum Methyljodid wesentlich geringer. An Stelle des Natriumthiosulfates, das durch seine Umsetzung mit Äthyljodid zu einem beachtlichen Analysendefizit führen würde, kann 10%ige Natriumantimonyltartrat-, 5%ige sodaalkalische Hydroxylaminchlorhydrat-, 5%ige Ascorbinsäure- oder 5%ige Hydrazinlösung als geeignete Waschflüssigkeit verwendet werden.

Die Frage, ob das in einer Alkylimid- oder Alkoxylbestimmung ermittelte Alkyljodid einer Methyl- oder einer Äthylgruppe entstammt, läßt sich unter Ausnutzung des sehr unterschiedlichen Ausmaßes der Umsetzung von wassergelöstem Natriumthiosulfat mit Methyl- bzw. Äthyljodid sicher entscheiden. Dieser Weg ist den für diese Frage bisher zur Verfügung stehenden Verfahren an Einfachheit überlegen.



## Summary.

By means of pure ethyl iodide weighed out in vials, it was shown that sodium thiosulfate dissolved in water also reacts with ethyl iodide under the conditions of the alkylimide- and alkoxyl determination. The extent of the reaction is considerably less in comparison with methyl iodide. A 10% solution of sodium antimonyl tartrate, or 5% alkali soda hydroxylamine hydrochloride solution, or a 5% ascorbic acid solution, or a 5% hydrazine solution can be used as suitable wash liquid in place of sodium thiosulfate, which because of its reaction with ethyl iodide can lead to a significant analysis deficit.

The question whether the alkyl iodide determined in an alkylimide or an alkoxyldetermination comes from a methyl or an ethyl group, can be definitely answered by means of the very different extent of the reaction of the water-dissolved sodium thiosulfate with methyl and ethyl iodide, respectively. This method of approaching this question is superior in simplicity to the procedure previously available.



## Résumé.

Par emploi d'iodure d'éthyle pur pesé dans des fioles, on a pu montrer que le thiosulfate de sodium dissous dans l'eau pouvait réagir aussi sur l'iodure d'éthyle dans les mêmes conditions que pour le dosage de l'alcoylimide et de l'alcoxyle. L'importance de la transformation est comparativement plus faible qu'avec l'iodure de méthyle. A la place du thiosulfate de sodium qui conduit à un déficit non négligeable à cause de son action sur l'iodure d'éthyle, on peut utiliser comme liquide de lavage approprié, une solution à 10% d'antimonyltartrate de sodium ou une solution sodique à 5% de chlorhydrate d'hydroxylamine ou à 5% d'acide ascorbique ou à 5% d'hydrazine.

La question de savoir si dans un dosage d'alcoylimide ou d'alcoxyle, l'iodure d'alcoyle mis en évidence provient d'un groupe méthyle ou éthyle

se laisse déterminer en tirant parti de l'action très différemment poussée du thiosulfate de sodium sur l'iodure de méthyle ou d'éthyle. Jusqu'ici, en raison de sa simplicité, ce moyen est considéré comme un procédé mis à la disposition pour la résolution de la question.

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# A New Method for the Determination of Sulphur in Organic Compounds Containing Nitrogen.

By

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There has always been a need for a convenient method for determining sulphur in organic compounds containing nitrogen. When halogens are present besides sulphur, reliable titrimetric methods can be applied successfully, but the presence of nitric acid or nitrates (resulting from the decomposition of certain nitrogen-containing substances) necessitates the use of a titrimetric method specific for sulphates. Until recently no such method having the requisite accuracy and convenience has been available.

The difficulties which arise when the conventional titrimetric methods for sulphate are applied are too well-known to mention in detail. Benzidine is useless on the micro-scale because of the high solubility of its sulphate and the fact that nitrate and even chloride ions interfere. Rhodizonic acid and its salts have never behaved satisfactorily in our hands; and in any case nitrate ion interferes, as is to be expected in any method in which a barium salt is used as titrant.

Other methods have been proposed in which the problem is avoided by departing from conventional procedure based on combustion in oxygen and absorption in a suitable liquid. For example, in the method of *Zimmermann*[1] the sulphur is converted to sulphide by fusion with metallic potassium and then determined iodometrically after evolution of hydrogen sulphide; or sulphur oxides have been absorbed on metallic silver to form silver sulphate which is then determined by some suitable means[2,3]. We do not intend to discuss here the merits of these methods, but will confine ourselves to the procedure most widely used in which the sample is burnt in oxygen or air in a combustion tube and the acid gases are absorbed in a suitable liquid absorbent. In this case the only means of obtaining an accurate result is to use the gravimetric barium sulphate

method after expelling nitrate by evaporation with hydrochloric acid. Certain titrimetric methods can be applied, but the evaporation cannot be avoided unless some loss in accuracy can be tolerated.

*R. Goulden*, working in this Department, examined six procedures which might be used to complete the determination. For convenience the assessment was made using standard sulphate solutions. The procedures and conclusions reached were as follows.

1. *Precipitation with barium chloride, evaporation to expel free acids and determination of the excess barium ions by the mercuric oxycyanide method*[4].

When smaller amounts of barium chloride were added (thus reducing the large back-titration of the original method), and sulphuric acid (which tended to obscure the end-point by precipitating barium sulphate in the back-titration) was replaced by nitric or perchloric acid, satisfactory results were obtained. They were not, however, quite as good as those obtained by the gravimetric method.

2. *Precipitation with barium chloride, then precipitation of the excess barium ions with standard iodate and finally titration of the residual iodate*[5].

The errors of this procedure were large owing to the solubility of barium iodate.

3. *Conversion of the sulphate to hydrogen sulphide by distillation in the presence of stannous chloride and phosphoric acid*[6].

On the micro-scale results were very unsatisfactory.

4. *Precipitation with barium chloride and back-titration with ammonium sulphate using barium rhodizonate as indicator*[7].

With slight modification, this method gave good results and the end-points were immeasurably superior to other rhodizonic acid indicators. However, nitrate interfered seriously and it was necessary to remove it by evaporation.

5. *Precipitation with hexamminocobaltic bromide*[8].

Good results were obtained when the sulphate was $> 4$ mg; around and below this level the results were low.

6. *Precipitation with barium chloride, then precipitation of excess barium as chromate and finally, after filtration, titration of the barium chromate*[9].

This method was satisfactory when the sulphate was $> 10$ mg; below this range erratic results were obtained. Nitrate ion also interfered.

It was concluded that procedures 1 and 4 were the most suitable for further examination (although evaporation to expel nitric acid was still necessary) and it was intended to investigate their possible application. In the meantime, however, as a result of our studies of substituted benzidines and related compounds we showed that certain aromatic monoamines possess sulphates whose solubilities are considerably less

than that of benzidine; the most promising was developed as a reagent for sulphate[10]. The normal sulphate of this compound — 4-amino-4′-chlorodiphenyl — has a solubility of 15 mg per litre (cf. benzidine sulphate — 98 mg per litre; barium sulphate — 2.5 mg per litre). The sensitivity of this new reagent towards sulphate ions differs little from that of barium chloride. Moreover, nitrates and halides do not interfere as is the case with the benzidine reagent. Precipitation is effected in the $p_H$ range 1–2.

The reagent was first tested on pure sulphate solutions with satisfactory results (Table I). Nitric acid and hydrogen peroxide had no effect on the recovery of sulphate (Table II). Sulphonal, sulphonal with excessive amounts of nitrobenzoic acid present and finally organic compounds containing sulphur and nitrogen

Table I. Pure sulphate solutions.

| $SO_4^{2-}$ present (mg) | $SO_4^{2-}$ found (mg) |
|---|---|
| 1.013 | 1.017; 1.017; 1.022 |
| 2.026 | 2.026; 2.024 |
| 3.039 | 3.031; 3.034 |
| 4.052 | 4.036; 4.058 |
| 5.065 | 5.054; 5.060 |
| 6.08 | 6.06; 6.07 |
| 7.09 | 7.08 |
| 8.11 | 8.09 |
| 9.12 | 9.11 |
| 10.13 | 10.15; 10.14 |

Table II. Recoveries in the presence of 10 mg nitrate and 1 ml 30% $H_2O_2$.

| $SO_4^{2-}$ present (mg) | $SO_4^{2-}$ found (mg) |
|---|---|
| 1.013 | 1.008; 1.008; 1.020 |
| 2.026 | 2.022; 2.027; 2.022 |
| 5.066 | 5.046; 5.060 |
| 10.13 | 10.13; 10.14 |

Table III. Microdetermination of Sulphur.

| Compound | wt. taken (mg) | Sulphur (%) | |
|---|---|---|---|
| | | Theoretical | Found |
| sulphonal | 1.476 | 28.09 | 28.12 |
| sulphonal | 2.683 | „ | 27.99 |
| sulphonal | 3.422 | „ | 28.03 |
| sulphonal | 3.777 | „ | 28.18 |
| sulphonal | 4.689 | „ | 28.03 |
| sulphonal + nitrobenzoic acid | 3.500 | „ | 27.94 |
| | 11.004 | — | — |
| sulphonal + nitrobenzoic acid | 4.382 | 28.09 | 27.96 |
| | 15.021 | — | — |
| sulphamic acid | 5.454 | 33.05 | 32.97 |
| sulphanilic acid | 4.094 | 18.51 | 18.57 |
| hydrazine sulphate | 3.365 | 24.63 | 24.51 |
| 4-amino-4′-bromodiphenylsulphate | 4.821 | 5.40 | 5.30 |
| thiourea | 3.044 | 42.13 | 42.13 |
| s-benzylthiouronium chloride | 3.926 | 15.82 | 15.94 |
| s-benzylthiouronium chloride | 5.729 | „ | 15.76 |

were then analysed. On the micro-scale combustion was effected using the apparatus of *Belcher* and *Ingram*[11]. The *Schöberl* apparatus was used for the semi-micro amounts. It will be seen (Tables III and IV) that satisfactory results were obtained.

Table IV. Semimicrodetermination of Sulphur.

| Compound | wt. taken (mg) | Sulphur (%) | |
|---|---|---|---|
| | | Theoretical | Found |
| sulphonal | 17.436 | 28.09 | 28.22 |
| sulphonal | 25.014 | „ | 28.27 |
| sulphonal | 23.737 | „ | 27.96 |
| sulphonal | 27.498 | „ | 28.18 |
| sulphonal + nitrobenzoic acid | 18.561 | „ | 27.90 |
| | 30.028 | — | — |
| sulphonal + nitrobenzoic acid | 26.916 | 28.09 | 27.94 |
| | 50.800 | — | — |
| sulphanilic acid | 21.473 | 18.51 | 18.60 |
| thiourea | 18.135 | 42.13 | 42.07 |
| s-benzylthiouronium chloride | 30.093 | 15.82 | 15.91 |
| 4-amino-4′-chlorodiphenyl sulphate | 35.625 | 6.34 | 6.29 |
| hydrazine sulphate | 27.274 | 24.63 | 24.72 |

## Experimental.

### A. Microdetermination of Sulphur.

*Reagents:* An approximately 0.3% solution of 4-amino-4′-chlorodiphenyl hydrochloride in 0.1 N hydrochloric acid prepared by dissolving with warming about 3.5 g of the hydrochloride in 7–800 ml of water containing the requisite amount of hydrochloric acid, filtering and diluting to 1 litre.

A mixed indicator consisting of 3 parts 0.04% aqueous solution of the sodium salt of phenol red and 2 parts 0.04% aqueous solution of bromothymol blue.

Standard sodium hydroxide solution 0.02 N.

*Procedure:* The washings from the absorber (about 30–40 ml) are collected in a 100-ml conical beaker and a small amount of filter paper slurry is added. The solution is then treated with 30–40 ml* of 4-amino-4′-chlorodiphenyl reagent and allowed to stand for 20–30 minutes.

Meanwhile, a glass funnel (diameter 1.5–2.0 inches) is prepared for the filtration as follows. The stem of the funnel is closed with one finger and the funnel three-quarters filled with distilled water. A small Witt plate (diameter $> 0.5$ inches) is placed in position in the neck of the

* 40 ml reagent suffice to precipitate a maximum of 3.5 mg sulphur as sulphate.

funnel, care being taken to ensure that any air bubbles held under the plate are completely removed. A slurry of filter paper fibre is added and the water allowed to drain from the stem. The depth of fibre in this pad should not be greater than 0.5 inches. The edges of the pad are gently pressed down, and, with the finger replaced on the end of the stem, a further amount of fibre slurry equal to about half that already used is added. The excess water is allowed to drain away, and, after gentle tamping, the pad is washed with water. If properly prepared, a column of water fills the part of the funnel below the plate, and filtration is rapid.

The contents of the precipitation vessel are transferred gradually to the filter. When all the mother liquor has passed through the pad, 4–5 ml of the filtrate are returned to the vessel and used to swirl out any appreciable amounts of precipitate remaining on the walls. The vessel is then washed out with 8–12 ml of distilled water in 3–4 portions, allowing the filter to drain before each fresh addition of wash liquid. Finally, the pad is washed with small amounts of distilled water until the washings give no turbidity with silver nitrate solution. (A further 4–5 ml usually suffice after completing the washing of the vessel.)

The funnel is drained under gentle suction and the upper part of the pad transferred to the precipitation vessel using a small stainless steel spatula. The remainder of the pad is used to remove particles of precipitate which adhere to the wall of the funnel. Finally, the funnel is washed with distilled water and the wash liquid collected in the vessel. The contents of the vessel (about 25–35 ml) are boiled for 1 minute and 3–4 drops of indicator solution are added. The hot solution is titrated with standard sodium hydroxide solution until the first permanent purple colour is apparent in the solution.

### B. Semi-microdetermination of Sulphur.

*Reagents:* An approximately 0.35% solution of 4-amino-4′-chlorodiphenyl hydrochloride in 0.05 N hydrochloric acid prepared using about 4.0 g of the substance as described above.

Indicator solution as in A.

Standard sodium hydroxide 0.05 N.

*Procedure:* The washings from the absorber (about 40–50 ml) are collected in a 200-ml conical beaker, a small amount of filter paper slurry and 80–100 ml* of reagent added.

A filter pad is made as described in A, using a funnel of 3 inches diameter, and a Witt plate of diameter $^3/_4$—1 inch. The depth of fibre

* 100 ml suffice to precipitate a maximum of 9—10 mg sulphur as sulphate.

in the funnel should be about $^3/_4$ inch. The procedure is then identical with A above to the stage where the precipitate is transferred to the precipitation vessel. Before diluting the contents of the vessel with the water used to wash the funnel, it is advisable, especially when large amounts of sulphate are present, to break up any aggregates of precipitate by thorough stirring of the pulp slurry. (If the pulp has been well drained, 2–3 ml of water are added). The determination is then continued as described above and the hot solution titrated with 0.05 N sodium hydroxide solution.

*Recovery of reagent:* The filtration and titration liquors are collected in a 5 litre flask. When almost full, the contents of the flask are made alkaline and filtered on a Büchner funnel. After washing with water and draining well, the residue of pulp is transferred to a 600-ml beaker, stirred up with 80–100 ml of methanol and again filtered. The pulp is then washed with 200–300 ml of diethyl ether and the filtrate distilled to remove the ether, which may be retained for further recoveries of reagent. The methanolic solution of 4-amino-4′-chlorodiphenyl is treated with 50 ml of 1 : 1 hydrochloric acid and boiled to dissolve the precipitated hydrochloride. On cooling, the pure hydrochloride is obtained as almost colourless, shimmering leaves. The material is filtered and dried. The filtrate may be returned to the residue vessel, or evaporated to about half its volume when a further amount of hydrochloride is obtained.

## Summary.

A new method is described for the micro- and semi-microdetermination of sulphur in organic compounds when nitrogen is also present. After combustion by conventional procedures, the sulphate formed is precipitated with 4-amino-4′-chlorodiphenyl, filtered and titrated alkalimetrically. Nitrates and halides do not interfere. The method is rapid and accurate.

## Zusammenfassung.

Eine neue Methode zur Mikro- und Semimikrobestimmung von Schwefel in stickstoffhaltigen organischen Verbindungen wird beschrieben. Das im üblichen Verbrennungsvorgang gebildete Sulfat wird mit 4-Amino-4′-chlordiphenyl gefällt, filtriert und alkalimetrisch titriert. Nitrate und Halogenide stören nicht. Das Verfahren ist rasch und genau.

## Résumé.

On décrit une nouvelle méthode micro et semimicro du soufre dans les composés organiques quand le soufre est présent. Après combustion par les procédés habituels, le sulfate formé est précipité par l'amino-4 chloro-4′diphényle, filtré et titré par alcalimétrie. Les nitrates et les halogénures n'interfèrent pas. La méthode est rapide et précise.

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# Microchemistry: An Appraisal*.

By

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The Committee of the *Microchemistry Group* recently made two decisions with which, I regret to say, I am in profound disagreement. Firstly, they decided that it was appropriate that there should be, at this meeting, for the first time in the history of the *Group*, a Chairman's Address. Secondly, they further decided that a desirable topic for me to present would be some consideration of the present state of microchemistry.

Having thus been "railroaded" into a difficult position, I feel that I ought to make quite plain my inadequacy for this task. There are many controversial aspects of microchemistry. I have thought about some of these; and have views on a few—views, I should perhaps warn you, that may well change from time to time. But I doubt if I have given sufficient philosophical study to most of these controversial topics to be able to appraise microchemistry with a balanced or a mature judgment.

Most of what follows, then, must be regarded as a process of thinking aloud, in a rather desultory way, about some aspects of that subject which brings us all together here—thinking which must make little pretence to produce unassailable answers or satisfying conclusions—thinking which may even, from time to time, be self contradictory.

* Chairman's Address to the Microchemistry Group of the Society of Public Analysts and Other Analytical Chemists, Great Britain, 29th January, 1953.

*Editor's Note:* In view of the fundamental content of this lecture, and its special interest for our readers, we are glad of the opportunity to publish it in "Mikrochimica Acta". After about half-a-century of microchemical work it appears most timely that the position of microchemistry should be reviewed.

Having presented this *apologia*, then, in terms that may make criticism kindly—since I cannot hope to disarm it completely—I must now, in fairness to your Committee, agree that this is, indeed, an appropriate time for a review of the progress of microchemistry. The Committee, as chemists so often do, has reached the right result using the wrong theoretical approach.

It is just 30 years since the first issue of "*Mikrochemie*" appeared, marking what might be called the coming of age of the subject. There can be infinite debate about the genesis of microchemistry, and credit has been awarded, with varying degrees of seriousness, to authors from *Pliny* onwards. *Benedetti-Pichler*[1] claims that the year 1899, in which *Friedrich Emich* read his inaugural Address as President of the Technische Hochschule in Graz, on the "Perfection of the Experimental Tools of the Chemist", marks the appearance of microchemistry as a definite concept. I myself have elsewhere[2] suggested 1909, on the appearance of the paper by *Emich* and *Donau* on the handling of small precipitates[3]. In 1901 and 1902 *Emich*[4] was working on the fibre technique which enabled confirmatory tests with a limit of identification of $10^{-10}$ g to be carried out. In 1903 *Nernst* and *Riesenfeld*[5] described the use of the *Nernst* balance for residue determinations on small samples. We can very well take some point within this range as our starting point, and assume that microchemistry, as an organised branch of chemistry, is now half a century old. It has, in other words, reached some measure of maturity. It is certainly no longer to be regarded as a young, relatively untried, rather noisy youngster, but as a well-proved member of the chemical community.

With this conclusion in mind it is impossible to resist quoting Professor *Strebinger*[6], in his introduction to the first number of "*Mikrochemie*": "Es ist noch nicht allzulange her, daß man der Mikroanalyse im allgemeinen skeptisch gegenüberstand und daß man ihren Anwendungsbereich auf jene Fälle beschränkt sehen wollte, in denen Materialmangel die üblichen Makromethoden zur Ausschaltung zwang; heute muß bereits für viele Teilgebiete der Analyse dieser Standpunkt als überwunden bezeichnet werden, da die Mikromethoden wegen ihrer Exaktheit bei ungleich rascherer Durchführung schon vor vielen Makromethoden den Vorzug verdienen."—"It is not very long since microchemistry was regarded, on the whole, with scepticism, and since its sphere of application was restricted to those cases where lack of material prevented the application of the ordinary macromethods. Today this point of view has been superseded in many branches of analysis, and many micromethods are preferred to the corresponding macromethods because of their precision and their rapidity."

What *Strebinger* wrote sprang undoubtedly from an enthusiastic and properly *propagandist* desire to bring enlightenment to those that

sat in outer darkness. The interesting thing is that today his words are almost precisely applicable in *calculated* terms, and have no necessity as a rallying call *pour encourager les autres.*

It is true that the methods of microchemistry still do not receive full appreciation in a few quarters: that there are still a few chemists who are ignorant of the important contribution that this branch has made to chemistry as a whole. But now, happily, these are the minority, not the majority.

Having considered at length how best to survey the field of microchemistry, it seemed to me that one possible way, and, to me, an attractive way of approach is interrogatively and adverbially! I felt that I ought to be able to supply some sort of answers to the queries, What? When? Who? Why? Where? and Whither?

Accordingly, I am going to look at each of these, although, in the case of some of them, very briefly.

It is unfortunate that of these headings the one which comes first logically, and without which no proper discussion of the others dare be made, is probably the most difficult of all. What is microchemistry? Until this is answered one is open to a charge of presumption in attempting to discuss applications or trends.

I can assure you that the full answer will not be supplied in this lecture. It is necessary, however, to look at some of the views which have been expressed, ranging from the inexcusably supercilious dismissal of "this *Pregl* stuff" which was used recently in my hearing by an analytical chemist who should have known better, to the over-enthusiastic assumption that a 25-ml titration only fails to be included in microchemical techniques by some inexplicable freak of nature!

Discussion of this point is rendered even more necessary by the rather startling assertion, made recently by one of the foremost exponents of the subject, that there is no such thing as microchemistry[7]. Much as I hesitate to disagree with Professor *Feigl*, I cannot accept his arguments on this point.

The designation "microchemistry", he claims, "is erroneous, because it denotes a contrast to a 'macrochemistry', which actually is non-existent. There are only micro- and macromethods of chemical analysis, of methods of preparation, etc."

It is, I think, necessary to examine rather more closely the reasoning by which he arrives at this conclusion. In discussing nomenclature he says: "Many names, including some which have come to be keywords, cannot withstand critical examination. For instance, the familiar term 'microchemistry' apparently was derived from 'microchemical study.' It is entirely logical to regard as microchemical work that which *Benedetti-Pichler* has recently fittingly referred to as the 'micro-technique of

general chemical experimentation.' This micro-technique has proved extremely useful for preparative chemistry, for experiments to determine the occurrence of certain chemical changes, for demonstration experiments, in analytical studies; as has been shown by actual experience, it is even decisive in the solution of certain problems. Nonetheless this extensive and significant application of the micro-technique, whose founding and development are scientific achievement of high order, cannot be stipulated as a necessary factor in the existence of a separate province of chemistry which bears the name 'microchemistry.' All special provinces of chemistry justify their existence either by dealing with certain groups of material or with special phenomena and regularities. A special field of microchemistry would exist even if it were concerned merely with phenomena and modes of behaviour different from those dealt with by 'macrochemistry'. However, this is not the case, and therefore the term 'microchemistry' is just as erroneous as the familiar designation 'technical chemistry' which eventually was replaced by 'chemical technology.'"

Now let us carry this argument to its logical conclusion. When we do so, we are immediately hesitant, for example, about "biochemistry;" for although this deals with special groups of materials, it does not concern itself with phenomena and modes of behaviour essentially different from those which are in the province of the physical chemist or the organic chemist. When it does, it ceases to be any part of chemistry and becomes instead physiology or some other branch of medical science.

But more particularly, Professor *Feigl*'s conclusions would condemn out of hand the use of the term "analytical chemistry," a term which he himself employs quite happily, and which he refers to elsewhere in the same paper as "one of the oldest divisions of chemistry."

Analytical chemistry neither deals with special groups of materials nor with special phenomena and regularities. In fact, it is a *sine qua non* that it concerns itself with *all* the materials of chemistry, indeed, all the materials of the universe; and that it deals with them by *any* phenomena whatsoever, chemical or otherwise, which it is able to press into service. This was recently stressed by *Ashley*[8] in a general consideration of the place of analytical chemistry, and has been put more picturesquely by *Clark*[9] and by *Elving*[10], who has said: "At present, all or most analytical chemists feel that the analytical method used is not as important as obtaining certain information and that in order to obtain that information one should use any technique which will give it, including... mediaeval history, if the latter will help us."

*Feigl* has used as an alternative, and, it may be, as a preferred term, "chemical analysis;" but chemical analysis is merely the embodiment of an ethos which is enshrined in analytical chemistry. The latter is, above all, a philosophy—an attitude of mind, which can, when required,

encompass mediaeval history together with all the other approaches. To my way of thinking, microchemistry, in exactly the same way on a smaller pattern (since microchemistry is to a considerable extent—though by no means wholly—a part of analytical chemistry), exactly in the same way microchemistry is primarily an *approach* which finds itself worked out in microtechniques. The microchemical concept of "chemical asepsis," for example, has often been quoted as one of the revolutionary contributions which have helped to place modern analytical chemistry, with its inevitable emphasis on trace analysis, in the position of importance which it holds today.

If, then, we accept, as I feel we must, the existence of a branch of chemistry known as "microchemistry," we may have some desire to indicate its boundaries. I referred earlier to the contemptuous phrase "this *Pregl* stuff." This might have been excused, though not justified, twenty years ago, when lack of knowledge led many people to assume that organic combustion methods constituted pretty well the whole operational field of the microchemist. Even if this exaggerated state of affairs did exist, we have recently been reminded[11] that at the present time the majority of organic analyses reported in the scientific journals are carried out by these methods, and that in consequence microchemical methods have a foremost importance for the worker in the field of natural products no less than for the atomic energy worker.

However, the fact of the matter is that a survey of the literature suggests that organic analysis has not received the attention, in the field of microanalysis, that its general importance warrants. In a recent year it was estimated[12] that 58 per cent of all papers published in the field of analytical chemistry were concerned with organic analysis. In order to get some comparable figures for microchemistry I surveyed the sources which might be said to represent most truly the responsible opinions and performance of a balanced body of microchemistry—the papers published in "*Mikrochemie*" and the papers read at meeting of the *Microchemistry Group*.

In "*Mikrochemie*," over its first six years, less than a quarter of the papers were concerned primarily with organic analysis, even using this term in a much wider sense than elementary and group analysis. In 1951, the volume publishing the proceedings at the *1st International Microchemical Congress* at Graz, the proportion was noticeably higher, but was nowhere near the 50 per cent mark. In this *Group*, perhaps one third of the papers have had an organic bias. We must remember that biochemical journals rightly carry a considerable proportion of microanalytical papers with an organic background, so that the position is not quite so unfavourable to the organic chemists as the figures would suggest. But I am quite sure that we are not pampering them. In the

annual reviews of organic and inorganic microchemistry presented by "*Analytical Chemistry*," only a quarter, or at best, three-eighths of the total references quoted are provided by the organic side.

A much more vexed question for those who have given serious thought to the scope of microchemistry is the attitude towards instrumental analysis. This is a very thorny problem, and one which I would probably be well-advised to avoid, but in fairness I must make some attempt to face up to it.

Most dispassionate commentators are quite certain that some instrumental methods contribute heavily to the field of microchemistry. *West*[13] has stated in forthright fashion that "microchemical analysis can be considered to include the sampling, separation, detection, and estimation of minute amounts of material, regardless of the techniques employed. Quite properly, emission spectrography, polarography, chromatography and similar techniques, which are fields within themselves, fall under the broad classification of microchemistry... The development of microchemistry is dependent on advances in instrument and apparatus design together with disclosures of new reagents, reactions, and techniques" and again[14], "Well over 60 per cent of the microchemical procedures involve colorimetry."

*Haagen-Smit*[11], in discussing microchemistry, refers to a wide range of instrumental and other methods, his discussion referring, in turn to gravimetric, titrimetric, colorimetric and biological methods, partition chromatography, counter-current distribution, chromatography, infra-red spectrography, mass-spectrography and X-ray diffraction.

The difficulty arises largely, as *Wenger*[15] has implied, through the rapid growth in importance of trace analysis. "*Emich* and *Pregl*," he says, "perfected techniques for quantities of the order of a milligram. A further problem is that of estimating trace impurities in amounts of material of the order of a milligram. Microchemistry must then follow an new development, by applying physicochemical techniques which modern science has placed at the disposal of the research worker... That is why we are in a period of intense development,... where the microchemist finally penetrates into all the new regions of analysis, making his own this ingenious and expensive equipment."

The critical diversity of opinion is, of course, found when one attempts to draw a sharp line of demarcation between those instruments which the microchemist may properly claim (and which the outsider will allow that he may claim) to employ, and those which he will admit take him outside his proper sphere of activity.

Perhaps the clearest classification up to the moment may be derived from the proposals made by *van Nieuwenburg*[16] (who is not primarily concerned with the definition of microchemistry as such, but with a distinction between classical and modern methods of analysis).

"It has been said," he points out, "that [the classical methods] differ from the modern methods in that they belong to the domain of chemistry, while modern methods are more closely allied to physics. In my opinion this is certainly not true. Finding the composition of a substance or of a mixture is always chemistry, whatever the means employed. Others say that the classical methods use chemical means and the modern methods physical means. This seems to me to be only partially true. Indeed, weighing a precipitate or reading a burette are no less physical acts than measuring a refractive index or reading a galvanometer scale... On the other hand one cannot deny that the 'chemistry-content' of the old methods is considerably higher than that of some instrumental methods. At one of the extremes we have an old-fashioned titration or a gravimetric determination, which as a rule requires quite a lot of manipulation, adding reagents, and generally changing the nature of the component molecules:... At the other end we find such non-destructive methods as X-ray diffraction analysis. The means used here are one hundred per cent physical; the molecules remain unchanged. If the term 'physical methods' is appropriate anywhere, it is here; but, let me emphasise, its object lies within the domain of analytical chemistry.

[With many of the instrumental methods] the brain-work is essentially of a chemical nature. It is not as if we could simply put a sample of an ore or an alloy into a slot and get out the complete analysis on the other side. Generally speaking, all the chemical operations remain the same as with the classical methods, only the tools we use at the end of the analysis are different. So it is evident that when comparing the old methods with the new ones, we cannot treat the latter all alike. Some of them, like spectrophotometric colorimetry, potentiometric analysis and polarography... are only new tools, while the framework remains the same; they are chips of the same block, more allies than rivals. On the other hand, we have procedures like emission-spectrography, X-ray analysis and mass-spectrography, which introduce fundamentally new ways of elucidating the composition of a substance. They not only change chemical analysis; they create a new branch of analytical chemistry."

*van Nieuwenburg* has in this way divided instrumental methods into those which are new tools of an old division, and those which are tools to be regarded as entering into a new branch of chemistry. This is a difficult concept, and even with *van Nieuwenburg*'s classification the dividing line may not always be distinct. However, I am content to assume that when the *scope* of any of the instruments in his italics category falls within the *range* of microchemistry, it may be regarded as a microchemical tool.

This mention of range, as opposed to scope, leads me to another controversial issue. Various definitions have been offered from time to time for the terms "macro", "semi-micro", "micro" and "ultramicro" as applied to chemical procedures. Most of these agree fairly well in terms of figures, but the real disagreement arises in deciding on their proper application. Recently a definitive statement has been issued[17] which recommends that the application be based on the *sample size* taken for analysis: thus, micromethods should refer to methods requiring a sample size from 10 mg down to 0.1 mg. This is a view from which many, I for one, must dissent; and once again, this diversity of opinion arises through the existence of trace analysis.

A more reasonable view is to assume that if, at any stage in a chemical procedure, the operations involve the manipulation of quantities in any of the small-scale ranges, then such procedure is within the ambit of the microchemist.

Thus it could properly be conceded that to carry out absorptiometric or polarographic analysis where the original sample weight was of the order of 1 g, and volumes of solution nowhere fall below 10 ml might be looked upon as a macrochemical procedure, even though the amount being estimated was of the order of a few parts per million. On the other hand, either of these estimations on a sample of 5 mg, or either of these estimations if, at any stage the volume had to be reduced to 1 ml and manipulated at this level, would allow a true microchemical classification.

This, however, is an assertion about which I would be even less dogmatic than any of those which I have already made!

The next of my interrogative adverbs is When? A thorough student, in his doctorate thesis of "The Development of the Modern Police Force," is reputed to have opened with the statement: "*Adam* was the first policeman." I have no doubt that on proper investigation it would be found that *Adam* was also the first microchemist. I have already mentioned that a case has been put for *Pliny*; and, with more justification, the work of *Margraaf*, *Raspail* and *Teichmann* has been cited by *Benedetti-Pichler*[1] as qualifying for priority in any consideration of claims. And *Gillis*[18] has recently reminded us that assaying methods which were quite sensitive were in use in the eighteenth century.

There are, however, a few early instances of micromethods which I would like to mention in more detail, not to make any claim for priority, but simply because I don't think that they are generally known. On the physicochemical side there is rarely any mention of *Wollaston*, who, when asked to show someone his laboratory, produced a small tray of apparatus; and who was the proud possessor of a "galvanic arrangement" —an electric cell—fitting into a tailor's thimble.

I myself have a more direct interest in the work of *Thomas Andrews*, first Professor of Chemistry in my own University. He used the polarising microscope in testing for sodium (present as chloride) by a test which he determined as being sensitive to less than 0.1 microgram[19]. In a paper published in 1855 on the Polar Decomposition of Water by Common and Atmospheric Electricity[20] he turned to gas analysis. Even as late as that date it had not been conclusively proven that electricity acting on water produced hydrogen at one pole and oxygen at the other. Indeed, *Faraday* believed that water was a special case, the molecules breaking down at both poles to produce both gases. After much experimentation *Faraday* apparently achieved true polar decomposition—that is, hydrogen at one pole and oxygen at the other: but with the minute amounts of gas produced he was not able to provide chemical proof. *Andrews* tackled this problem, using an electrical machine producing only 0.00006 ml of gas per minute, and showed the chemical nature by a serious of ingenious experiments. Collecting the gas in thermometer tubing, he measured the relative amounts of each gas. He then showed that electric sparks through one tube gave the colour characteristic of hydrogen; while sparks through the other tube caused a diminution in volume, following which the test for ozone with potassium iodide gave a positive result. Finally, reversal of the terminals reversed the relative additional amounts of the gases; and the mixture thus obtained could be exploded by a spark.

Above all, I would like to draw your attention to a state of affairs which existed in Edinburgh at least as early as 1833. In giving evidence before the Select Committee on Education in Ireland, in 1835, Dr. *D. B. Reid* described his class in practical chemistry. Dr. *Reid* was a forceful supporter of the teaching of chemistry by practical class work only—a novel enough idea at that time. But it is the detail of the equipment which is of interest here[21].

"The students were arranged along five boards, each being provided with twenty gas-lamps, one of which was placed alternately on either side. Every pupil received a blowpipe, a test tube, slips of paper on which tests were applied, and also a broad and narrow slip of glass such as glaziers throw away. These slips were used for the same purposes as the paper, [that is, tests were applied on them] and also for solution, boiling, evaporation, crystallisation, and filtration: the narrow slips, on the other hand, were employed for imitating furnace operations, heat being applied by a common lamp or candle, assisted, where this was necessary, by the blowpipe."

Reactions were observed, if necessary, through the microscope, but this is not, you will note, just chemical microscopy, usually acknowledged as the oldest systematic branch of microchemistry. It is true microchemical qualitative technique, and is, near enough, an apt

description of this type of work even at the present time. At a time when we are apt to preen ourselves on our up-to-dateness in introducing small-scale techniques into our classes, it is, I think, salutary to be reminded that in *Reid*'s textbook[22] he lists apparatus and chemicals suitable for science teaching in *schools* which included this microchemical apparatus, and which, he claimed, should not cost more than £ 3. A portable set of apparatus based on *Reid*'s list was on sale in Dublin during the fifth meeting of the British Association (1835) at £ 1 11s 6d. I am not, of course, suggesting that all *Reid*'s teaching was by small-scale methods. But as he made his living by his private classes, the more students he could pack into a given space the better; and he had clearly realised the economic reasons for small-scale work as well as the instructional value of them. Indeed, the description already quoted[21] continues: "Experiments conducted in this manner were equally economical and effectual in communicating instruction; and the professional student might also, in the same way, repeat again and again, at home, at the most trifling expense, the greater number of those illustrations which he might see in the lecture-room... Every schoolmaster might provide himself with an apparatus sufficient to show thousands of experiments on the small scale, and awaken the minds of his pupils so as to take an interest in science." Apart from the slightly nineteenth century flavour of the language, this might be an extract from any article on the teaching of small-scale methods in chemistry written in the past twenty years.

On the subject of Who? I propose to remain discreetly silent. A few names spring immediately to mind. I have mentioned some of these earlier in various connections. But the task of presenting what must be a partial answer is one which justice compels me to postpone—for another 100 years, when accusations of unfair discrimination are not so likely to be levelled at me! In the year 2053 I will devote an hour or so to this question alone, for such of you as care to listen!

There is little to say that is not obvious, and that has not already been said many times over, on the subject of Why? The shortage of material that first drove *Pregl* to develop methods for the characterisa ion of minute amounts of the degradation products of desoxycholic acid is the reason that has ensured the application of these methods throughout the whole natural-products field. The concomitant saving in time and space, which was only fully realised on the subsequent development of semi-micro methods, is another very forcible answer. Economy in time, space and materials has equally been a factor in fostering small-scale teaching methods, but, as a teacher myself, I should like to emphasise that this is not the only reason that makes me support such teaching—in the field, for example, of qualitative analysis. I am thoroughly convinced that teaching small-scale methods serves a fundamental pedagogical

purpose in addition to the purely utilitarian one. *West*[23] claims that the methods seem to aid the development of a faculty for analytical chemistry, through the early introduction of better defined manipulative requirements. My own experience is that ingenuity and originality are encouraged, and interest is stimulated more certainly through these methods than through the older methods on the macro scale. And *D. B. Reid*—120 years ago—seems to have had no doubt on this score!

My remarks on Why?—Why did microchemistry develop, and why is it applied where it is?—also present the answers to Where? In teaching, research and routine analysis microchemical methods are now thoroughly established, and there is little further that is worth saying on this point to an audience of microchemists.

I have purposely left myself little time to deal with my final heading. Whither? That the field of analytical chemistry has felt the forcible impact of microchemistry already is obvious from the fact that smaller samples tend to be used, and trace determination is a normal procedure even where the work is not strictly micro work. The sensitivities of some of the newer methods are such as could not have been anticipated 50 years ago. Fluorescence analysis at $10^{-10}$ g: nephelometry at $10^{-8}$ g: polarography, with its recent extensions, using a rotating mercury cathode, from the order of 1 in $10^6$ to somewhere in the region of 1 in $10^7$—$10^8$: radioactive techniques at 1 in $10^{12}$ to the astounding figure of 1 in $10^{18}$ in favourable cases: ultramicro gravimetric analyses with a sensitivity of $pD = 8$ because of the ability to deal quite comfortably with smaller and smaller samples (perhaps as small as $10^{-5}$ or $10^{-6}$ g) on a quantitative basis; these are now accepted almost as a matter of course. There is undoubtedly available for investigation, therefore, a whole field of *submicrogram* procedures which will take advantage of the ever-extending sensitivities, of the "scaling-down" procedures, and of the introduction of new techniques.

Microchemistry—*ordinary* microchemistry, if I can call it that—will almost be a firmly established older cousin, and one, too, which has exerted its influence on every branch of the chemical family. To microchemists the *new* techniques may become the intriguing fiddling of specialists—or cranks—that microchemistry was to the general analyst 50 years ago!

My contention is that the development of a new technique often makes evident the need, rather than the reverse. Many problems were shirked, shelved or ignored because, until microchemistry came along, they had no hope of solution. Now any average laboratory regards ability to tackle microchemical problems as one of its normal functions. In the same way, when submicrogram procedures have been developed, we will almost certainly find uses for them in ways which we cannot even visualise at the moment.

*Haagen-Smit*[11] has said that "the widespread use of microchemistry in all branches of chemistry and biology has made the microanalytical chemist of the past the analytical chemist of today." This is a very sweeping statement—too sweeping to be accepted even by enthusiastic microchemists, for there are still vast non-micro aspects of analytical practice. But there is sufficient truth in his remark to give microchemists cause for satisfaction with the assured place of their subject; and sufficient justification to arouse the ire, rather than the contempt, of the non-microchemist!

**Summary.**

The early history of microchemistry supports the view that this branch of chemistry has now reached the half-century mark. It is now fully established as a scientific field, and it is of interest to review its nature, origins and present position, and to glance briefly at its probable future development.

Justification is held for the use of the term "microchemistry". The scope of microchemical work, both in the classical and the instrumental fields, is outlined with reference to recently expressed views in other publications. Some early, but not well-known, instances of microchemical work are quoted, in particular an example of teaching in the early nineteenth century using small-scale methods. The reasons for the present use of microchemistry, and some likely trends in its future use are briefly surveyed.

**Zusammenfassung.**

Die Geschichte der Mikrochemie umfaßt nunmehr ein halbes Jahrhundert, das die Ausgestaltung dieses Zweiges der Chemie zu einer eigenen Wissenschaft mit sich brachte. Es scheint von Interesse, deren Anfänge und Eigenart sowie ihren gegenwärtigen Stand zu betrachten und ihre vermutliche Weiterentwicklung zu erwähnen. Die Bezeichnung „Mikrochemie" sollte beibehalten werden. Die Merkmale mikrochemischer Arbeitsweise in methodischer und instrumenteller Hinsicht werden gegenüber Auffassungen, die kürzlich von anderer Seite veröffentlicht wurden, gekennzeichnet. Frühere, weniger bekannte mikrochemische Arbeiten, besonders ein Beispiel der methodischen Verwendung kleiner Substanzmengen für Zwecke des Unterrichtes zu Beginn des 19. Jahrhunderts werden hervorgehoben. Die gegenwärtige Pflege und Anwendung der Mikrochemie werden begründet und die wahrscheinliche Richtung ihrer künftigen Anwendung diskutiert.

**Résumé.**

Les débuts de l'histoire de la microchimie sont en accord avec le fait que cette branche de la chimie a maintenant un demi-siècle d'existence. Elle est actuellement établie comme un champ scientifique et il est intéressant de faire une revue de sa nature, de ses origines et de son état actuel et de jeter rapidement un coup d'oeil sur son développement probable dans l'avenir.

On donne une justification sur l'emploi du terme «microchimie». Les domaines du travail microchimique à la fois sur les terrains classiques et instrumentaux sont mis en relief avec référence à des vues exprimées récemment dans d'autres publications. On a noté quelques aspects énoncés depuis longtemps, mais mal connus du travail microchimique, en particulier, un exemple d'enseignement du début du 19ème siècle utilisant des méthodes sur une petite échelle. On passe rapidement en revue les raisons pour l'emploi présent de la microchimie et quelques tendances vraisemblables pour son avenir.

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# Some Further Absorption Properties of Manganese Dioxide.

By

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## Introduction.

It has been established that manganese dioxide at room temperature retains oxides of nitrogen quantitatively for its use in the microdetermination of carbon and hydrogen[1]. A further study of the absorption properties of the compound has now been carried out for the purpose of establishing other uses of the reagent in microcombustion methods of elemental analyses.

The reagent was first employed to determine the percentage conversion of nitrogen to oxides of nitrogen following combustion of organic compounds by the rapid combustion procedure. The present work was undertaken for two reasons: (1) to investigate the extent of formation of nitrogen oxides in types of compounds where the nitrogen is linked to carbon, hydrogen and oxygen, and (2) to attempt the determination of nitrogen by its conversion to nitrogen dioxide and subsequent gravimetric estimation.

Because a simple method for the simultaneous determination of carbon, hydrogen and halogen would be desirable, the possibility of using manganese dioxide for the retention of chlorine and bromine externally was next explored. The experiments showed that chlorine was retained quantitatively by the reagent, whereas bromine was not. For obvious reasons it was not considered practical to attempt iodine absorption.

Finally, sulphur-containing compounds were burned to study the behaviour of the combustion products on the water absorption tube, prior to their removal by manganese dioxide.

## Experimental.

### *Apparatus.*

A combustion train of the type described earlier[2] was employed for the combustion experiments. The horizontal quartz tube contained only the plug of quartz wool situated in the front end of the hot zone, which was maintained at 900° C. The manganese dioxide was contained in a *Flaschenträger* absorption tube for the gravimetric estimations, and in a U-tube for the qualitative tests. The reagent was prepared as before[1], and the fillings were backed by a short layer of Anhydrone.

### *Combustion Procedure.*

Before each series of tests, the efficiency of the combustion train was checked in the normal way by means of blank tests and by combustion of standard substances. The normal rapid combustion procedure was followed, using an oxygen flow rate of 50 ml per minute.

### *The Oxidation of Nitrogen During Combustion.*

In these experiments the various compounds were burned (1) in the empty tube, and (2) in the presence of platinum gauze which was introduced into the combustion tube in the form of a roll 15 cm long. A cooling chamber was placed before the weighed absorption tube containing the manganese dioxide. In some of the experiments silver gauze was also placed in the tube, and in others the cooling chamber was not inserted in the absorption system. The results of these experiments are given in Table I. The percentage conversion found under the conditions specified indicate that platinum induces the formation of nitrogen dioxide, and that the amount produced depends on the form of nitrogen linkage. In addition, it is apparent that silver does not retain oxides of nitrogen. This confirms the findings of *Heron*[3], who has carried out similar experiments, but under different conditions, and has also employed a colorimetric procedure to determine the concentration of nitrogen dioxide. With a combustion tube packed with silica chips and containing silver, he found that for the amino compounds examined the nitrogen dioxide conversion was between 1 and 17% of the total nitrogen; for heterocyclic compounds the conversion was between 7 and 40%; and for nitro compounds was between 82 and 97 per cent. That the present results are more consistent is possibly attributable to the better control of combustion conditions. *Heron* used a flow rate of between 25 and 30 ml. This was maintained by continual adjustment of the control tap of an evacuated bottle attached to the exit of the combustion tube. The combustion products were collected in the bottle and the nitrogen oxides retained for subsequent determination colorimetrically.

Table I.

| Conditions of test | Compound | Sample weight mg | mg $NO_2$ | % N | % N required | % N conversion |
|---|---|---|---|---|---|---|
| (1) | *m*-Dinitrobenzene | 3.504 | 1.16 | 10.1 | 16.66 | 61 |
| (2) | | 3.181 | 1.12 | 10.7 | | 64 |
| (3) | | 4.06 | 1.00 | 7.57 | | 45 |
| (4) | | 3.599 | 1.90 | 16.06 | | 96 |
| (2) | Picric acid | 3.61 | 1.32 | 11.1 | 18.34 | 61 |
| (3) | | 3.772 | 1.08 | 8.71 | | 48 |
| (4) | | 2.986 | 1.73 | 17.6 | | 96 |
| (4) without silver | | 4.019 | 2.25 | 17.05 | | 93 |
| (2) | Dimethylglyoxime | 3.48 | 1.205 | 10.5 | 24.1 | 43 |
| (4) | | 3.334 | 2.03 | 18.5 | | 76 |
| (2) | *p*-Diacetoxy- | 3.46 | 0.12 | 1.05 | 9.5 | 11 |
| (4) | azobenzene | 3.732 | 0.315 | 2.56 | | 27 |
| (4) without silver | | 3.758 | 0.305 | 2.46 | | 26 |
| (1) | Azobenzene | 4.834 | 0.11 | 0.69 | 15.4 | 4.5 |
| (2) | | 6.196 | 0.14 | 0.69 | | 4.5 |
| (4) | | 5.34 | 0.225 | 1.27 | | 8.2 |
| (2) | $\alpha:\alpha'$-Dipyridyl | 4.23 | 0.075 | 0.54 | 17.9 | 3 |
| (4) | | 4.021 | 0.145 | 1.09 | | 6.1 |
| (2) | *p*-Tolunitrile | 5.93 | 0.13 | 0.66 | 11.95 | 5.5 |
| (4) | | 3.605 | 0.17 | 1.43 | | 12 |
| (2) | Phenacetin | 4.066 | 0.13 | 0.97 | 7.82 | 12 |
| (4) | | 4.089 | 0.42 | 3.12 | | 40 |
| (4) without silver | | 3.655 | 0.44 | 3.65 | | 47 |
| (2) | Urea | 6.588 | 0.20 | 0.92 | 46.6 | 2 |
| (4) | | 4.76 | 0.565 | 3.6 | | 8 |

(1) Empty tube; (2) Silver present; (3) No Cooling Chamber; (4) Platinum present.

Other experiments were made by burning *m*-dinitrobenzene in a *Friedrich* train and using a flow rate of oxygen of 5 ml per minute. The percentage conversion was between 85 and 98 per cent, which indicates that the flow rate condition is not an important factor. Attempts to obtain higher conversion rates, by passing the combustion products through the hot zone of the tube packed with platinised asbestos, failed. Since 100 per cent conversion was not obtained the determination of nitrogen in nitro compounds by combustion and subsequent weighing of the nitrogen dioxide produced was not practicable.

*The Absorption of Halogens by Manganese Dioxide.*

A small U-tube was packed with granules of the reagent, and chlorine mixed with purified air was passed through at 5 ml per minute. For this a 100-ml reservoir was used, and an air–chlorine ratio of 5:2 was employed. Starch-iodide solution contained in a bubbler attached to the outlet of the U-tube served to indicate the presence of chlorine in the issuing gas stream. A dilute air–bromine mixture was tested in a similar manner. The tests indicated that chlorine was held by the manganese dioxide, whereas bromine was not, and poisoned the filling.

*Quantitative Tests.*

For these, the rapid combustion train was blanked, and the water, manganese dioxide and carbon absorption tubes weighed. Then samples of *p*-chloro-benzoic acid were burned and the weight increase of the tubes determined. The results showed that none of the halogen combustion products were retained in the water absorption tube; and that all the chlorine was retained by the manganese dioxide, since the carbon figures were correct to within the allowed error. Further, the weights of chlorine collected agreed satisfactorily with the theoretical values. The results are given in Table II. Next, samples of D. D. T. [1.1.1-trichloro-2.2-bis(*p*-chlorophenyl)ethane] were analysed using a U-tube filled with manganese dioxide. Satisfactory carbon and hydrogen figures were obtained. This confirmed that the procedure may be used for the simultaneous determination of carbon, hydrogen and chlorine in samples which contain no other elements producing combustion products retained by the reagent.

Table II.

| Compound | Sample weight | Found % C | Found % H | Found % Cl |
|---|---|---|---|---|
| *p*-Chlorobenzoic acid .. | 3.45 | 53.78 | 3.49 | 22.6 |
| 53.7% C<br>3.19% H ..... | 3.942 | 53.85 | 3.05 | 22.45 |
| 22.7% Cl..... | 3.621 | 53.8 | 3.26 | 22.52 |
| D. D. T. ..... | 4.077 | 47.36 | 2.52 | |
| 47.4% C..... | 3.25 | 47.6 | 2.65 | |
| 2.6% H ..... | 3.96 | 47.3 | 2.71 | |
| | 6.285 | 47.58 | 2.75 | |

When bromine containing samples were analysed, high carbon values were obtained due to some bromine being carried over into the soda-asbestos absorption tube.

*The Combustion of Sulphur Containing Compounds.*

In the experiments sulphur compounds were burned in the rapid combustion apparatus in the same way as in the chlorine analyses. Sulphur combustion products were retained by the weighed tube containing manganese dioxide. The carbon and hydrogen figures were satisfactory, but small and varying weights of sulphur dioxide were obtained well below the expected values. On examination of the cooler parts of the combustion tube adjacent to the beak, some sulphuric acid was found, indicating that the sulphur combustion products consist largely of the acid. Some results are given in Table III. They indicate that sulphur combustion products such as sulphur dioxide are not retained in the water absorption tube, but are retained by the manganese dioxide placed between the water and carbon dioxide absorption tubes.

Table III.

| Compound | Sample weight | Found % C | Found % H |
|---|---|---|---|
| Acetylsulphanilamide ..... | 3.765 | 44.97 | 4.82 |
| 44.9 % C ..... | 3.761 | 44.95 | 4.89 |
| 4.68% H ..... | 4.182 | 44.73 | 4.86 |
| Sulphonal ..... | 4.326 | 36.91 | 7.13 |
| 36.8 % C ..... | 3.69 | 36.85 | 7.02 |
| 7.06% H ..... | 5.328 | 36.73 | 7.19 |
| | 2.866 | 36.68 | 7.23 |

Other experiments were carried out to determine to what extent nitrogen would interfere in the titration of sulphuric acid produced by absorbing the sulphur combustion products in neutral hydrogen peroxide solution. For these tests the apparatus designed for the determination of sulphur by the rapid combustion procedure was employed[4]. The oxygen was dried by means of Anhydrone. Nitrogen-containing compounds were burned and the combustion products passed through the bead absorber containing neutral hydrogen peroxide. The amount of acid produced was then determined by titration with 0.01 N sodium hydroxide solution. These results are given in Table IV. The screened indicator, methyl red-methylene blue, was bleached from the neutral colour to bright green during the course of the determinations. Before the titration, the solution obtained was boiled for a few seconds to remove carbon dioxide. Further indicator solution was then added to show the normal colour change.

Analysis of acetylsulphanilamide by the above procedure occasionally gave almost theoretical sulphur figures, but some high results were

obtained indicating that small amounts of nitrogen products were also retained in the bead absorber. The equivalent due to this absorption was about 0.2 ml of 0.01 N sodium hydroxide. Further combustions of 10–100 mg samples of urea yielded acid equivalents of between 0.2 to 0.4 ml of 0.01 N sodium hydroxide. Therefore, one may assume that the yield of nitrogen oxides is not dependent on the percentage of nitrogen or the amount (in milligrams) in the sample.

Table IV.

| Compound | Sample weight mg | ml of 0.01 N NaOH |
|---|---|---|
| Phenacetin | 4.363 | 0.015 |
| Urea | 8.059 | 0.019 |
| | 10.45 | 0.08 |
| | 46.89 | 0.23 |
| | 73.6 | 0.35 |
| | 110.5 | 0.42 |
| p-Tolunitrile | 3.60 | 0.03 |
| $\alpha:\alpha'$-Dipyridyl | 5.992 | 0.2 |
| Dimethylglyoxime | 5.865 | 0.26 |
| Nitron | 7.030 | 0.7 |
| $\alpha$-Nitroso-$\beta$-Naphthol | 6.462 | 0.79 |
| Picric acid | 3.20 | 0.65 |

## Conclusions.

The results of the oxidation tests indicate that platinum induces the oxidation of nitrogen to an extent depending on the linkage of the nitrogen in the compound. Thus, under conditions of the carbon and hydrogen determination, the presence of N—H or N—C linkages will result in a conversion of between 1 to 10 per cent; and nitro compounds show a conversion of about 60 per cent. Compounds containing $=NOH$ groups, *e. g.*, dimethyl glyoxime, appear to yield a lower value than nitro compounds. With platinum present these values are increased markedly: a N—H or N—C linkage yields conversion figures varying between 8 to 50 per cent, and nitro compounds yield almost all their nitrogen as nitrogen dioxide. With compounds containing $=NOH$ groups the values are again lower. In the case of an N—H linkage it appears that the amount of nitrogen dioxide produced is similar, whether the nitrogen content is small, as in phenacetin, or large, as in urea. This accounts for the large difference in the conversion values for phenacetin and urea burned in the presence of a catalytic surface of platinum.

It is evident that manganese dioxide could be applied to determine nitrogen dioxide derived from other sources provided halogens and sulphur dioxide were absent.

Whereas the reagent cannot be applied to determine carbon, hydrogen, and nitrogen simultaneously, chlorine may be determined together with carbon and hydrogen provided that other interfering elements are absent. It is assumed that chlorine is adsorbed by manganese dioxide.

The experiments concerned with the sulphur estimation confirm the findings of *Beet* and *Belcher*[5]. These authors found that interference from nitrogen oxide retention was negligible in their rapid method for sulphur and halogens in coals. Since large samples of 0.5–1 g were taken, and it was found in the present investigation that only small fractions of nitrogen products were retained by the peroxide absorption solution, the amount would be too small to affect the results obtained. In the microdetermination however, the amount of nitrogen products retained would appreciably affect the accuracy of the sulphur or halogen figure.

## Summary.

The percentage conversion of nitrogen to nitrogen dioxide has been determined by burning organic compounds under rapid combustion conditions. Manganese dioxide has been employed to determine the yield of nitrogen dioxide by a gravimetric procedure, thus increasing the accuracy of the method of determination. The conversion is never complete.

It has also been established that manganese dioxide quantitatively retains chlorine. This property has been utilised to determine carbon, hydrogen and chlorine simultaneously, following the rapid combustion procedure. Evidence has been obtained that if sulphur dioxide escapes retention by silver situated in the combustion tube, then it will be retained by the manganese dioxide and will not interfere with the carbon figure. Both sulphur dioxide and chlorine are not retained in the water absorption tube.

The amount of nitrogen oxide retention by neutralised hydrogen peroxide has been investigated in connection with the determination of sulphur by the rapid combustion procedure. Retention, though small, affects the result, but this is negligible when macro samples are burned, because the amount retained does not increase markedly with size of sample or nitrogen content.

## Zusammenfassung.

Der Anteil Stickstoffdioxyd, der aus dem Stickstoff organischer Substanzen unter den Bedingungen der Schnellverbrennung gebildet wird, wurde gravimetrisch mit Hilfe von Mangandioxyd bestimmt. Die Genauigkeit der Analysenmethode konnte dadurch verbessert werden. Stickstoff wird hierbei niemals vollständig zu Stickstoffdioxyd oxydiert.

Weiters wurde festgestellt, daß Chlor quantitativ von Mangandioxyd gebunden wird. Von dieser Tatsache wurde zur gleichzeitigen Bestimmung

von Kohlenstoff, Wasserstoff und Chlor Gebrauch gemacht. Sofern Schwefeldioxyd nicht vom Silber innerhalb des Verbrennungsrohres festgehalten wird, wird es gleichfalls von Mangandioxyd gebunden und beeinträchtigt daher die Kohlenstoffwerte nicht. Weder Schwefeldioxyd noch Chlor werden im Wasserabsorptionsröhrchen zurückgehalten.

Das Ausmaß der Stickoxyd-Absorption in neutralem Wasserstoffperoxyd bei der Schwefelbestimmung nach dem Schnellverbrennungsverfahren wurde untersucht. Die allerdings geringfügige Absorption beeinflußt jedoch die Ergebnisse. Doch ist dies zu vernachlässigen, wenn Makroeinwaagen verbrannt werden. Denn die Menge absorbierten Stickstoffdioxyds wird bei höheren Einwaagen oder Stickstoffgehalten nicht merklich größer.

**Résumé.**

Le pourcentage de conversion de l'azote en bioxyde d'azote a été déterminé en brûlant des composés organiques dans des conditions de combustion rapide. Le bioxyde de manganèse a été utilisé pour déterminer le rendement de bioxyde d'azote par un procédé gravimétrique, augmentant ainsi la précision de la méthode de dosage. La conversion n'est jamais complète.

Il a aussi été établi que le bioxyde de manganèse retient quantitativement le chlore. Cette propriété a été utilisée pour doser le carbone, l'hydrogène et le chlore simultanément, suivant le procédé de combustion rapide. On a montré que si le gaz sulfureux échappe à la rétention par l'argent situé dans le tube à combustion, il sera retenu par le bioxyde de manganèse et n'interfèrera pas avec le nombre trouvé pour le carbone. Le gaz sulfureux et le chlore ne sont pas retenus dans le tube absorbeur d'eau.

La rétention de l'oxyde d'azote par l'eau oxygénée neutralisée a été étudiée en connexion avec le dosage du soufre par le procédé de combustion rapide. La rétention, quoique faible, affecte le résultat, mais ceci est négligeable quand on brule des macro-échantillons du fait que la quantité retenue n'augmente pas d'une façon marquée avec les dimensions de l'échantillon ou la teneur en azote.

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# Eine Methode zum Nachweis und zur Bestimmung organischer Säuren in Papierchromatogrammen.

Von

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Mit 3 Abbildungen.

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Obwohl die Zahl der Arbeiten über papierchromatographische Trennungen einiger Stoffklassen sehr groß ist, wurde diese Methode bisher nur verhältnismäßig selten zur Trennung organischer Säuren eingesetzt. Dies dürfte seinen Grund in erster Linie darin haben, daß die bisher zur Verfügung stehenden Nachweismethoden weder die Empfindlichkeit der für den Nachweis von Aminosäuren und Zuckern verwendeten Reaktionen besitzen, noch hinsichtlich allgemeiner Anwendungsmöglichkeit, Zeitaufwand und deutlicher Sichtbarkeit der Flecke mit jenen konkurrieren können.

Zur Entwicklung organischer Säuren auf dem Papier werden meistens $p_H$-Indikatoren verwendet. Diese sind im allgemeinen nur anwendbar, wenn mit flüchtigen *basischen* Lösungsmitteln chromatographiert wurde. Bei Verwendung *saurer* Lösungsmittelgemische sind sie dagegen wenig geeignet, da die Chromatogramme vor dem Sprühen auch von letzten Lösungsmittelspuren befreit werden müssen, wozu extrem langes Trocknen notwendig ist. Die unten angegebene *Silbernitrat-Phenol-Methode* unterliegt dieser Beschränkung nicht und ist sowohl für *basische* wie für *saure* Lösungsmittel anwendbar.

Bisher wurden für die Entwicklung der Chromatogramme folgende Methoden vorgeschlagen:

a) Nach Chromatographie mit *basischen* Lösungsmitteln.

*Brown* und *Hall*[1] chromatographieren Fettsäuren mit Ammoniak enthaltenden Lösungsmitteln und trocknen 5 Minuten bei 95°. Nach Besprühen mit Bromkresolgrün erhalten sie gelbliche Flecke auf blaßblauem, bzw. mit Bromthymolblau auf grünlichem Grund. Die Erfassungsgrenze für Citronensäure nach dieser Methode fanden wir bei 10 $\mu$g.

In einer späteren Arbeit zieht *Brown*[2] die Trocknung im Dampftrockenschrank vor und entwickelt mit Bromkresolgrün. Als Erfassungsgrenze werden 5 $\mu$g/2 $\mu$l angegeben, doch weist der Autor selbst darauf hin, daß das rasche Ausbleichen der Flecke von Nachteil ist.

*Hiscox* und *Berridge*[3] besprühen das ammoniakalische oder äthylaminhaltige Chromatogramm sofort mit Bromkresolgrün und lassen an der Luft einige Stunden trocknen. Die Salze der Fettsäuren erscheinen allmählich als blaue, rasch ausbleichende Flecke auf grünlichgelbem Grund.

*Reid* und *Lederer*[4] sprühen mit einer alkoholischen Lösung von Bromkresolpurpur, die mit Formaldehyd versetzt ist. Die gelben Flecke auf purpur werden dadurch besser sichtbar. Die Erfassungsgrenze für Citronensäure fanden wir bei 5 $\mu$g, allerdings bleichen die Flecke auch nach dieser Methode sehr rasch aus.

*Kennedy* und *Barker*[5] trocknen 5 Minuten bei 100° und sprühen mit einer Lösung, die 50 mg Bromphenolblau und 200 mg Citronensäure in 100 ml Wasser enthält. Es resultieren blaue Flecke auf gelbem Grund. die wesentlich besser zu erkennen sind als gelb auf blau. Wir konnten mit dieser Methode 0,31%ige Lösungen von Citronensäure (7.8 $\mu$g 2.5 $\mu$l) noch deutlich erfassen, 0,16%ige Lösungen. ebenfalls ein Tropfen zu 2,5 $\mu$l aufgebracht, nicht mehr.

*Long*, *Quayle* und *Stedman*[6] trocknen die ammoniakalischen Chromatogramme verschiedener organischer Säuren 15 Minuten bei 80° und sprühen mit BDH-Universalindikator. Keine Angaben über die Empfindlichkeit.

*Schlögl* und *Siegel*[11, 12] sprühen mit Umbelliferon und können im UV-Licht bis zu 20 $\mu$g organische Säuren als dunkle Flecke auf hellblau leuchtendem Untergrund nachweisen.

b) Nach Chromatographie mit *sauren* Lösungsmitteln.

*Lugg* und *Overell*[7] empfehlen, viele Stunden an der Luft zu trocknen und dann mit Bromkresolgrün oder Bromphenolblau zu besprühen. Je 20 $\mu$g Äpfel-, Wein- oder Citronensäure seien noch nachweisbar. Beim Nacharbeiten zeigte sich, daß 14stündiges Trocknen an der Luft für das Gemisch Essigester-Eisessig-Wasser (3:1:1) noch zu kurz war und der Bogen beim Besprühen einheitlich gelb gefärbt wurde.

*Denison* und *Phares*[8] trocknen vor einem Vielfach-Dampfentwickler (steam-manifolder) und bestrahlen gleichzeitig von der Rückseite mit U-Rot-Strahlern. Essigsäure soll sich in 5 bis 10 Minuten verflüchtigen. Ameisensäure in 15 Minuten. Die Autoren geben 0,2 $\mu$g-Äquivalente als noch nachweisbar an, entsprechend zirka 8 bis 18 $\mu$g.

*Buch*, *Montgomery* und *Porter*[9] sprühen mit ammoniakalischer Silbernitratlösung, trocknen bei Raumtemperatur und beobachten nach 4 Stunden weiße Flecke auf schwach lohfarbenem Grund. Als Optimum sprechen die Autoren 150 $\mu$g pro Fleck an.

Die vorhandenen Entwicklungsmethoden für saure Chromatogramme sind also nicht sehr befriedigend. Es haben sich aber für die Trennung organischer Säuren mit Hilfe der Papierchromatographie besonders saure Lösungsmittelgemische als recht gut geeignet erwiesen. Wir haben das System *Essigester—Eisessig—Wasser* für diesen Zweck näher untersucht; es soll in diesem Zusammenhang kurz darüber berichtet werden.

## Das System Essigester—Eisessig—Wasser als Lösungsmittelgemisch zur Trennung organischer Säuren.

Essigesterhaltige Lösungsmittel besitzen eine sehr große Steiggeschwindigkeit auf Filtrierpapier. Ihre Verwendung bietet eine beträchtliche Zeitersparnis gegenüber den sonst üblichen Gemischen. Das von *Denison* und *Phares*[8] vorgeschlagene Gemisch Äther-Eisessig-Wasser (13:3:1) steigt wohl noch etwas rascher, ist aber wegen des hohen Dampfdruckes des Äthers schon etwas unbequem zu handhaben.

Die $R_f$-Werte in Essigester enthaltenden Lösungsmitteln unterscheiden sich so stark voneinander, daß praktisch die gesamte Steighöhe des Lösungsmittels von $R_f = 0{,}00$ bis $R_f = 0{,}90$ zur Trennung ausgenützt wird.

Das Dreistoffsystem besitzt zwar bei Raumtemperatur eine Mischungslücke, doch ist sie relativ klein; es kann daher die Zusammensetzung des Lösungsmittelgemisches in weiten Grenzen variiert und den jeweiligen Bedürfnissen der Trennung angepaßt werden.

Wir verwendeten einphasige Gemische und arbeiteten nach der aufsteigenden Methode von *Williams* und *Kirby*[10] in gut schließenden Gefäßen. Da einer der Hauptvorteile dieses Lösungsmittels in der raschen Laufzeit liegt, wurde darauf verzichtet, eine Gleichgewichtseinstellung abzuwarten. Die Berechtigung dafür ergaben Parallelversuche mit bzw. ohne Einstellung des Gleichgewichtes. Die gefundenen $R_f$-Werte sind in Tabelle 1 zusammengestellt. Sie stellen Mittelwerte aus je drei Versuchen dar.

Tabelle 1.

| Säure | ohne Gleichgewichtseinstellung | mit Gleichgewichtseinstellung | Mittlere Abweichung |
|---|---|---|---|
| Äpfelsäure | 0,49 | 0,51 | + 0,02 |
| Bernsteinsäure | 0,78 | 0,78 | 0,00 |
| Citronensäure | 0,38 | 0,41 | + 0,03 |
| Glycerinphosphorsäure | 0,16 | 0,17 | + 0,01 |
| Malonsäure | 0,61 | 0,62 | + 0,01 |
| Milchsäure | 0,77 | 0,76 | — 0,01 |

Über die Abhängigkeit der $R_f$-Werte von der Zusammensetzung des Lösungsmittels gibt die Abb. 1 Auskunft. Hoher Gehalt an Essigester bedingt niedrige $R_f$-Werte. Steigender Essigsäure- oder Wassergehalt erhöhen sie. Mit steigendem Wassergehalt werden die Flecke schärfer, mit steigendem Essigsäuregehalt verwaschener und neigen zur Schwanzbildung. Sinkt der Essigestergehalt unter 50%, so ist der Trenneffekt infolge der dann schon durchwegs sehr hohen $R_f$-Werte nicht mehr groß. Die günstigste Trennwirkung für die üblichen Pflanzensäuren besitzt das System Essigester—Eisessig—Wasser im Verhältnis 5:2:1 (vgl. Abb. 2). Da es aber infolge der relativ hohen Eisessig-Konzentration verhältnismäßig große Flecke gibt, wurde das in bezug auf seine Trennschärfe ähnliche Gemisch 3:1:1 vorgezogen.

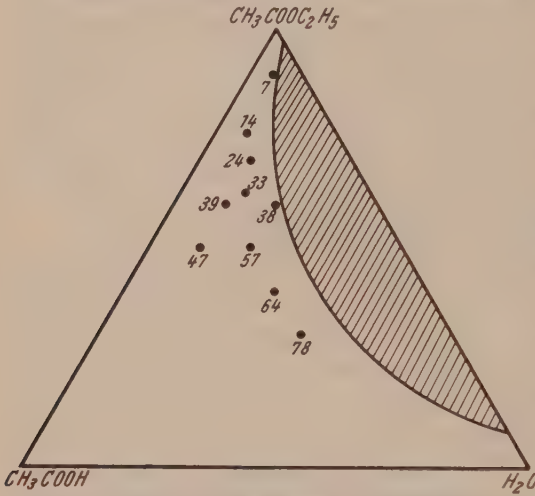


Abb. 1. $R_f$-Werte von Citronensäure in Abhängigkeit von der Zusammensetzung des Lösungsmittels.

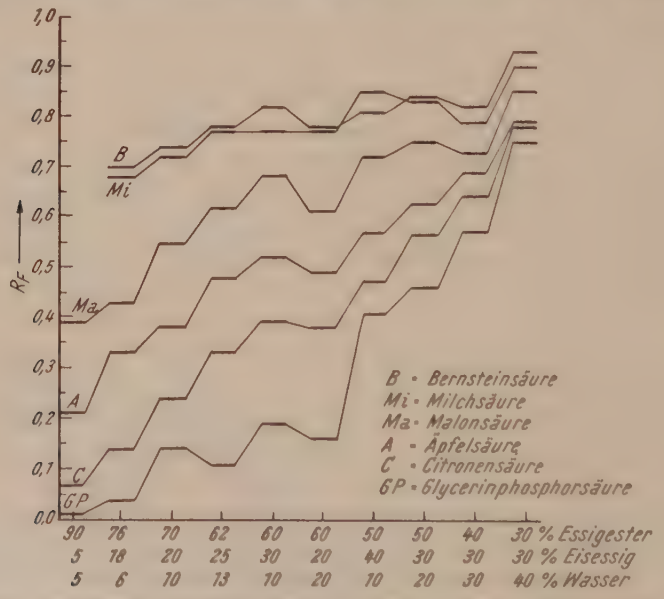


Abb. 2. Trennwirkung des Systems Essigester—Eisessig—Wasser für einige Säuren.

Die in Tabelle 2 angeführten $R_f$-Werte wurden nach folgender Arbeitsmethode erhalten: Das zu einem Zylinder zusammengerollte Papier (Schleicher & Schüll 2043b) wurde in eine Petrischale mit dem Lösungsmittel (3:1:1) gestellt. Die Startlinie befand sich 2 cm über dem Flüssigkeitsspiegel. Ein Glaszylinder mit einem nur wenig größeren Durchmesser als die Petrischale wurde darüber gestellt und für gasdichten Abschluß gesorgt. Laufzeit 200 Minuten. Steighöhe 20 cm. Raumtemperatur.

Tabelle 2.

| Säure | $R_f$ | Aminosäure | $R_f$ |
|---|---|---|---|
| Schwefelsäure | 0,08 u. 0,23 | Lysin | 0,06 |
| Glycerinphosphorsäure | 0,16 | Cystin | 0,08 |
| Phosphorsäure | 0,17 | Arginin | 0,12 |
| Weinsäure | 0,26 | Histidin | 0,15 |
| Citronensäure | 0,38 | Asparaginsäure | 0,15 |
| Ascorbinsäure | 0,44 | Threonin | 0,17 |
| Maleinsäure | 0,46 | Glutaminsäure | 0,20 |
| Äpfelsäure | 0,49 | Glycin | 0,20 |
| Malonsäure | 0,61 | Alanin | 0,28 |
| Gallussäure | 0,66 | Methionin | 0,37 |
| Aconitsäure | 0,70 | Valin | 0,37 |
| Brenztraubensäure | 0,70 | Tyrosin | 0,38 |
| Milchsäure | 0,77 | Isoleucin | 0,46 |
| Bernsteinsäure | 0,78 | Leucin | 0,47 |
| Lävulinsäure | 0,94 | Phenylalanin | 0,49 |
| | | Tryptophan | 0,49 |

Für die Trennung organischer Säuren mit hohen $R_f$-Werten eignen sich Gemische mit mehr Essigester besser. Bernsteinsäure und Milchsäure sowie Brenztraubensäure und Aconitsäure lassen sich im eindimensionalen Chromatogramm nicht trennen. Für die Trennung von Aminosäuren ist dieses Lösungsmittel wenig geeignet, es sei denn man arbeitet im Durchlaufchromatogramm.

**Entwicklungsmethode für Papierchromatogramme organischer Säuren.**

*Reagenzien.*

Lösung 1: 0,1-n Silbernitratlösung.

Lösung 2: Gleiche Teile wassergesättigtes Phenol und 0,05-n Natronlauge werden gut durchgeschüttelt. Verwendet wird die phenolreiche (untere) Phase.

*Ausführung der Entwicklung.*

Das Chromatogramm wird 5 Minuten im Trockenschrank bei 105 bis 110° getrocknet, mit Lösung 1 besprüht, so daß es gleichmäßig feucht

(durchscheinend) ist, aber nicht tropft, und wieder bei 105 bis 110° getrocknet. Auf dem Papier zeigen sich meist schon einige Säureflecke als weiße Stellen auf ganz schwach ockerfarbigem Grund; reduzierende Säuren (Ameisen-, Gallus-, Ascorbinsäure) geben sich als braune Flecke zu erkennen. Das vollkommen trockene Papier wird nun mit Lösung 2 schwach besprüht und erwärmt. Nach wenigen Sekunden bräunt sich die ganze Fläche mit Ausnahme der Säureflecke, die rein weiß auf tief orange-ockerfarbigem Grund erscheinen.

*Fehlerquellen.*

War das Papier vor dem Sprühen mit Lösung 2 nicht vollkommen trocken, so färbt sich der Untergrund graubraun bis dunkelgrau; die Säureflecke sind aber trotzdem gut erkennbar. Wird das Chromatogramm nach Sprühen mit Lösung 2 zu lange erwärmt, kann es überentwickelt werden, wodurch Flecke geringer Säurekonzentration unter Umständen dunkel und damit unerkennbar werden. Es empfiehlt sich daher, während der Entwicklung zu beobachten und kleinere Flecke (entsprechend geringen Säurekonzentrationen) noch während der Entwicklung mit Bleistift zu umranden. Bei Verwendung phenolhaltiger Lösungsmittel tritt innerhalb einiger Stunden ein allmähliches Nachdunkeln ein, bei Verwendung basischer Lösungsmittel innerhalb einiger Tage, während bei sauren Lösungsmitteln die Flecke noch wochenlang deutlich sichtbar bleiben. Zur Bereitung von Lösung 2 kann das Phenol ersetzt werden durch Resorcin, Anilin, Formaldehyd oder ähnliche schwach reduzierende Substanzen, doch ist Phenol hinsichtlich der Empfindlichkeit der Reaktion am geeignetsten. o-Phenylendiamin, p-Aminophenol und ähnliche, in der Photographie verwendete Entwickler sind unbrauchbar.

*Anwendungsbereich.*

a) *Lösungsmittel.*

Die Methode dürfte für alle Lösungsmittelgemische brauchbar sein, die für die Chromatographie organischer Säuren in Frage kommen, mit Ausnahme jener, die Silbernitrat reduzieren, also aller Kombinationen, die Ameisensäure enthalten. Von den bisher verwendeten Gemischen: Butanol-Eisessig-Wasser, Äther-Eisessig-Wasser, Essigester-Eisessig-Wasser, Phenol-Wasser, Äthanol-Ammoniak, Phenol-Ammoniak, Äthanol-Pyridin-Wasser, Essigester-Pyridin-Wasser, Phenol-Pyridin-Wasser, verursachte keines irgendeine Störung beim Entwickeln.

b) *Säuren.*

Folgende Säuren wurden nach Chromatographieren mit Eisessig enthaltenden Lösungsmitteln mit der beschriebenen Methode bisher von uns nachgewiesen: Aconit-, Äpfel-, Asparagin-, Bernstein-, Brenztrauben-,

Citronen-, Gallus-, Glutamin-, Glycerinphosphor-, Lävulin-, Malein-, Malon-, Milch-, Phosphor-, Schwefel-, Weinsäure.

Flüchtige Fettsäuren sind bei Verwendung saurer Lösungsmittel nicht mehr aufzufinden. Sie sind prinzipiell nachzuweisen, wenn sie als Salze aufgebracht und mit basischen Lösungsmitteln chromatographiert werden (auch Salzsäure und Salpetersäure sind dann nachzuweisen), doch ist für flüchtige Fettsäuren das Verfahren von *Reid* und *Lederer*[4] oder das von *Kennedy* und *Barker*[5] vorzuziehen.

*Empfindlichkeit.*

Die Erfassungsgrenze variiert mit der Natur der Säure. Citronensäure ist — unabhängig vom Lösungsmittel, mit dem chromatographiert wurde — in 0,078%iger Lösung noch sehr deutlich nachzuweisen, nicht mehr dagegen aus 0,039%iger Lösung, wenn ein Tropfen mit einem Volumen von 2,5 $\mu$l auf das Papier gebracht wurde. Die Erfassungsgrenze für Citronensäure liegt also bei zirka 1,2 $\mu$g. Phosphorsäure ist in 0,035%iger Lösung noch deutlich, in 0,017%iger Lösung nicht mehr nachzuweisen. Erfassungsgrenze: bei 0,5 $\mu$g. Milchsäure macht die größten Schwierigkeiten. Kleinere Mengen als 12 $\mu$g sind mit der Methode, wie sie oben beschrieben wurde, nicht mehr deutlich nachweisbar.

*Zeitbedarf.*

Der Zeitbedarf hängt ab von der Flüchtigkeit des verwendeten Lösungsmittels. Im allgemeinen beträgt er, gerechnet vom Herausnehmen des Papiers aus dem Trog bis zum fertigen Chromatogramm, 15 bis 25 Minuten.

*Quantitative Auswertung.*

Die allgemein angenommene Proportionalität zwischen Fleckengröße und Logarithmus der Konzentration konnte bestätigt werden, allerdings nur als Grenzgesetz für kleine Substanzmengen (vgl. Abb. 3). Bei größeren Mengen als zirka 30 $\mu$g Citronensäure waren die Flecke größer als dieser Beziehung entspricht. Die Fleckengröße ist abhängig von der Natur der Säure, von der Art des verwendeten Lösungsmittels und von der Laufstrecke der Lösungsmittelfront. Für Citronensäure in Essigester-Eisessig-Wasser (3:1:1) bei einer Steighöhe von 15 cm ergab sich als Mittelwert folgende Gerade:

$$\log m = 0{,}557\, f - 0{,}017$$

(vgl. Abb. 3), wobei $m$ die Substanzmenge in $\mu$g und $f$ die Fleckengröße in cm² bedeutet. Diese Gleichung ergibt als theoretische Erfassungsgrenze eine Menge von 0,96 $\mu$g.

Der mittlere Fehler bei der quantitativen Auswertung beträgt, wenn man nur einen einzigen Fleck mit der Testgeraden vergleicht, $\pm$ 10%. Er läßt sich auf $\pm$ 5% herabdrücken, wenn man folgendermaßen vorgeht: Man stellt von der zu untersuchenden Lösung eine Verdünnungsreihe her (jede Lösung von der halben Konzentration der vorhergehenden), chromatographiert und mißt die entstehenden Flecke aus. Dann trägt man die gefundenen Werte mit einer beliebigen Anfangskonzentration in das

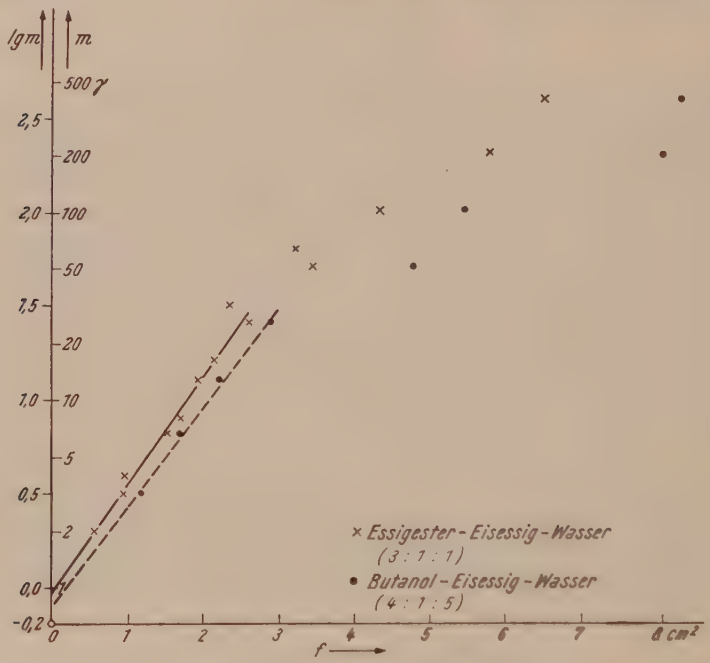


Abb. 3. Testgerade für Citronensäure.

Diagramm ein und bestimmt graphisch oder durch Ausgleichsrechnung jene Parallele zur Testgeraden, die sich den gefundenen Werten am besten anpaßt. Durch Parallelverschiebung ergibt sich dann sofort die gesuchte Konzentration.

Für grobe Schätzungen gibt schon die Bestimmung der Erfassungsgrenze einen guten Anhaltspunkt. Man chromatographiert eine Verdünnungsreihe und stellt fest, bei welchem Verdünnungsgrad die Säure eben noch nachweisbar ist. Das Mittel aus dieser und der nächstfolgenden Verdünnung entspricht mit 20 bis 30% Genauigkeit der Erfassungsgrenze der betreffenden Säure, woraus sich dann leicht auf die ursprüngliche Konzentration rückschließen läßt. Diese Schätzung ist genauer als der Vergleich eines einzigen Fleckes mit Testflecken verschiedener Konzentration.

## Zusammenfassung.

Es wird eine neue, allgemein anwendbare Entwicklungsmethode für Papierchromatogramme organischer Säuren angegeben, bei der die Säuren als reinweiße Flecke auf braunem Grund sichtbar gemacht werden. Die Erfassungsgrenze für Citronensäure liegt bei 1,2 $\mu$g, für Phosphorsäure bei 0,5 $\mu$g. Vergleich der Fleckengröße mit einer für die betreffende Säure und das verwendete Lösungsmittel aufzunehmenden Testgeraden erlaubt eine quantitative Bestimmung mit einem mittleren Fehler von $\pm$ 10%. Durch Herstellen einer Verdünnungsreihe der zu untersuchenden Lösung, Auswerten und Vergleich mit der Testgeraden läßt sich eine quantitative Bestimmung mit einem mittleren Fehler von $\pm$ 5% durchführen.

Das Dreistoffsystem Essigester—Eisessig—Wasser wird auf seine Eignung als Lösungsmittelgemisch für die Papierchromatographie organischer Säuren untersucht. Es eignet sich im Verhältnis 3:1:1 zur Trennung der in Pflanzen vorkommenden Säuren.



## Summary.

A new method of developing paper chromatograms of organic acids is given. It is generally applicable. The acids are made visible as pure white flecks on a brown background. The identification limit for citric acid is 1.2 $\mu$g, for phosphoric acid 0.5 $\mu$g. Quantitative determinations are possible through comparison of the size of the fleck with a test straight line constructed for the particular acid and solvent; the accuracy is $\pm$ 10%. A quantitative determination with a mean error of $\pm$ 5% can be made by preparing a dilution series of the solution being studied, valuating, and comparing with the test straight line. The three component system—acetic ester, glacial acetic acid, water—was studied with respect to its suitability as a solvent mixture for the paper chromatography of organic acids. In the ratio 3:1:1 it is suitable for separating the acids occurring in plants.



## Résumé.

On donne une nouvelle méthode utilisable, en général, pour révéler les chromatogrammes sur papier, d'acides organiques, dans laquelle ceux-ci sont rendus visibles à l'état de tache blanche sur fond brun. La limite de dilution pour l'acide citrique est voisine de 1,2 $\mu$g et celle de l'acide phosphorique de 0,5 $\mu$g. La comparaison de la dimension des taches avec une droite d'étalonnage pour l'acide correspondant et le dissolvant utilisé permet une évaluation quantitative avec une erreur moyenne de $\pm$ 10%. Par préparation d'une série de dilutions de la solution étudiée, estimation et comparaison à la droite d'étalonnage, un dosage peut s'effectuer avec une erreur moyenne de $\pm$ 5%. Le système triple ester acétique—acide acétique—eau a été étudié du point de vue de sa convenance comme mélange dissolvant pour la chromatographie d'acides organiques sur papier. Il convient pour la séparation des acides existant dans les végétaux si on le prend dans le rapport 3:1:1.

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From the Norwood Technical College, Knight's Hill, London.

# Some Developments in Microchemical and General Apparatus.

By

**J. T. Stock** and **M. A. Fill.**

With 41 Figures.

*(Received March 26, 1953.)*

Forming Stand C. 65 in the Analytical Techniques and Apparatus Section of the International Congress on Analytical Chemistry at Oxford, 1952, the exhibit to be described was arranged by invitation of the Microchemistry Group of the Society of Public Analysts and Other Analytical Chemists. Owing to shortage of space, only part of the available apparatus could be set up for continuous inspection. There were six sections, viz. stirring and allied devices, equipment for inorganic qualitative analysis, organic apparatus, electrochemical techniques, volumetric apparatus, and miscellaneous devices. To save space, all references quoted are to publications by the authors or their co-workers. Many of these publications contain full bibliographies or other acknowledgements.

## I. Stirring and Allied Devices.

The *agitator* shown in Fig. 1 is operated by a filter pump and is applicable to any mobile relatively non-volatile liquid, such as paraffin in a melting-point bath[1]. The side tube has a partially-constricted orifice which is set a few mm below the static level of the bath. On applying suction, liquid is drawn in through both orifices until a fall in bath-level allows air to enter through the side tube, causing a sudden fall in the level within the agitator. The bulk of the liquid flows from the lower orifice, restoring the bath-level and causing a repetition of the cycle. Continued

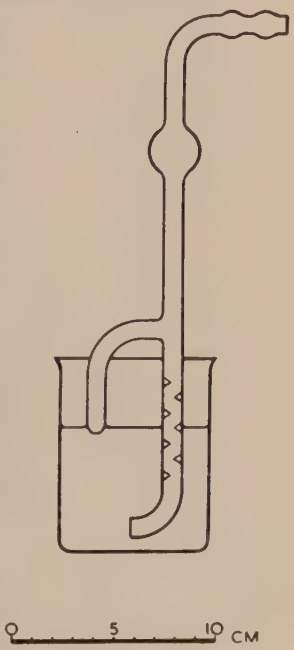



Fig. 1. Suction-Operated Agitating Device.

transference from top to bottom of the bath thus occurs with slight up-and-down motion of the liquid surface.

A feature of the *stirrer* shown in Fig. 2 is the free movement of the mercury and float A over most of the stroke[2]. Application of filter-pump suction to side tube *B* causes the mercury and float to rise in the guide tube. Not until considerable momentum has been acquired does the float strike and drive upwards valve rod *C*, thus producing the

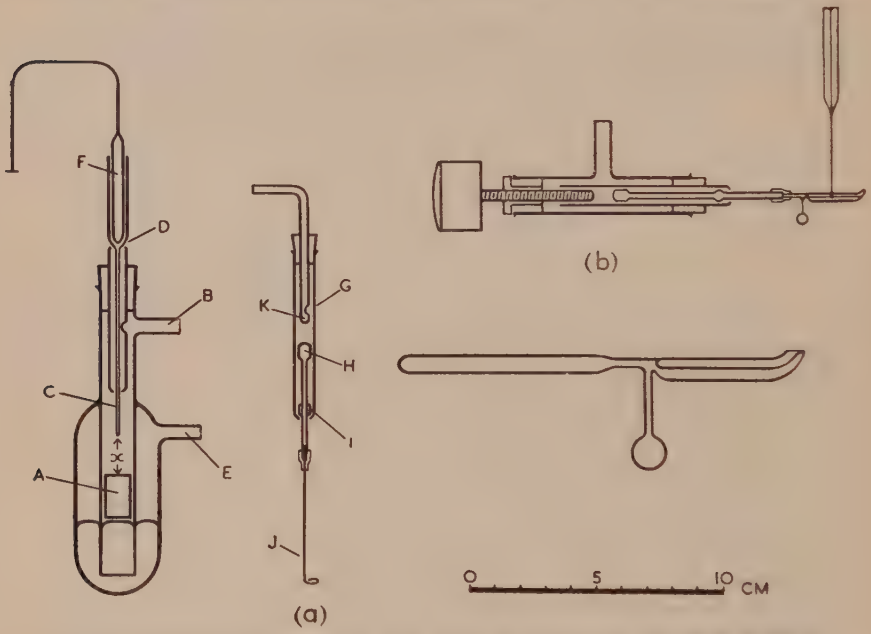



Fig. 2. Reciprocating Micro-Stirrer (*a*) slave stirrer (*b*) slave stirrer with stroke adjustable whilst running.

stirring motion and breaking the vacuum by opening valve *D*. When their momentum is expended, the moving parts fall by gravity, closing the valve and causing the cycle to be repeated. Using 10 to 15 ml of mercury, the frequency is about 4 strokes per second. This may be increased by about 50% by closing side tube *E*. By adjustment of rest position clearance *x* the stirrer stroke may be varied between 1 and 10 mm; increasing *x* increases the stroke. Drawn from glass rod, the interchangeable stirrer head *F* slips into the hollow valve head. The "impact" principle not only produces self-starting action but also renders it completely reliable; at no time during a continuous run of nearly 200 hours was the missing of a single stroke actually observed.

The mercury-pulsations in the outer portion of the stirrer unit will operate a "*slave*" *stirrer* through several feet of rubber tubing connected

to side tube *E*. This is useful, since the "slave" shown at (*a*) will operate in any position[3]. Cylinder *G*, of 6-mm bore glass tubing, has one end slightly constricted, the other end being slightly flared. Piston *H* is formed on the closed end of a length of 3-mm outside diameter tubing by thickening up into a ball 7 mm in diameter and grinding into the cylinder to an easy fit. Sleeve *I*, of cycle valve rubber tubing, limits the outward movement of the piston; a similar sleeve retains stirrer head *J*. The stroke is adjusted by altering the position of inner stop *K*. A modification shown carrying a "titration spoon" at (*b*) permits stroke adjustment during actual operation of the stirrer.

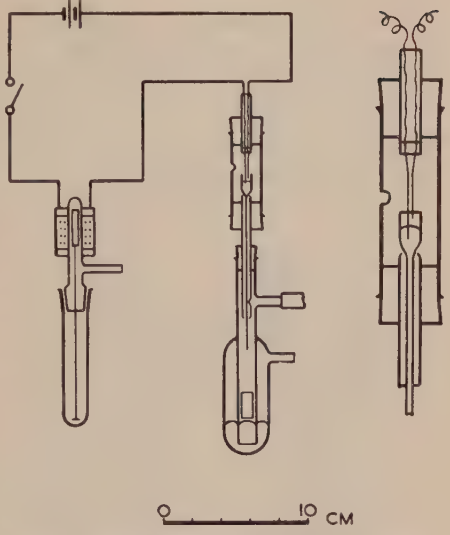



Fig. 3. Solenoid-Operated Stirrer with Suction-Operated Make-and-Break.

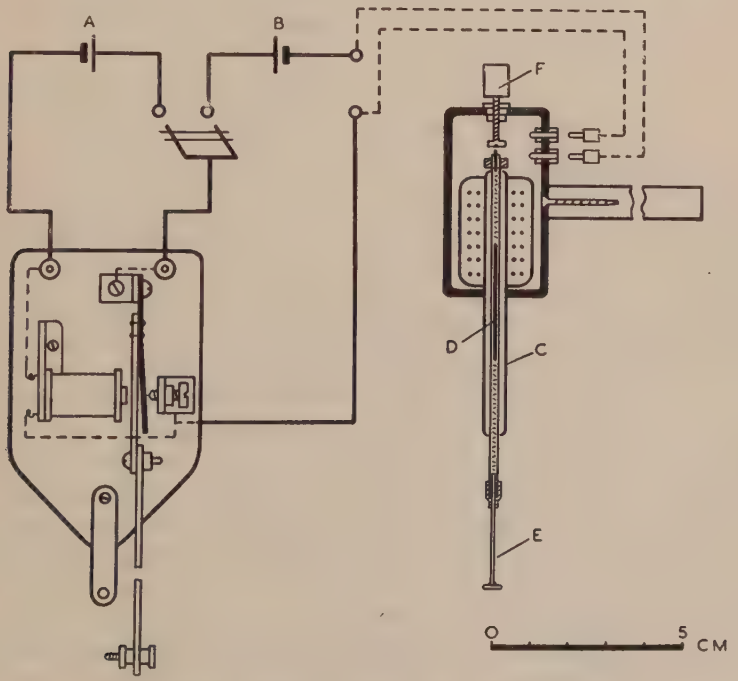



Fig. 4. Electromagnetic Micro-Stirrer and Impulse-Generator.

Modified as shown in Fig. 3, the unit may be used for driving a *solenoid-operated stirrer*. A bead of mercury placed in the valve head bridges the contacts each time the valve rises[4]. Another *electromagnetic micro-stirrer* utilises an electric bell movement as the impulse-generator[5]. By replacing the hammer with a loaded strip of bakelite, as shown in Fig. 4, the period of the contact-breaker is increased to about 0.3 sec. Accumulator *A* maintains the vibrations, whilst a second accumulator *B* energises the stirrer solenoid each time the contacts close. The stirrer body consists of two "Bakelite" reagent-bottle caps bolted mouth-to-mouth. Guide tube *C*, on which the solenoid is wound, is of glass tubing and is cemented in the rear cap. An iron nail with the head removed is wedged within and near the top of stirrer stem *D*. When the breaker contacts close, the nail is drawn upwards into the solenoid, lifting stem and stirrer head *E*. Knob *F* permits alteration of stroke whilst the stirrer is running. An alternative impulse-generator employing a modified telephone relay; and various other stirrer units were also exhibited.

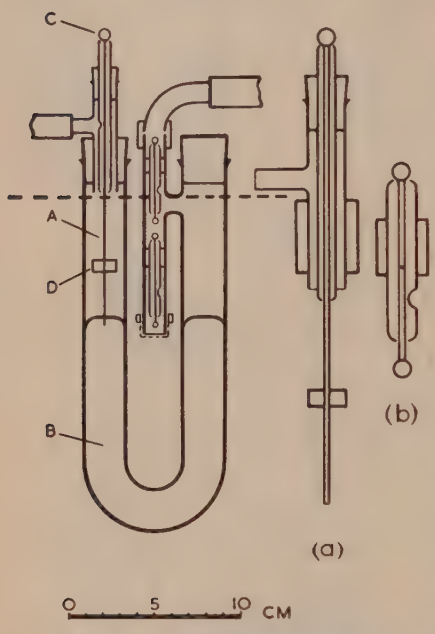



Abb. 5. Suction-Operated Water-Circulating Pump (*a*) vacuum valve (*b*) one of water valves.

A valve motion similar to the "impact" principle described above is used in the *suction-operated pump* developed for mounting in a thermostat bath to provide a feed for jacketed instruments[6]. Valve rod *A* (Fig. 5) tends to float when the mercury in limb *B* has risen to about 5 mm above its rest position. Floating is however prevented by atmospheric pressure on valve *C*. The continued rise of mercury causes sudden encounter with rubber bumper *D*, driving the valve off its seat and breaking the vacuum. The buoyancy of the valve rod causes it to rise several cm until, floating in the mercury, it follows the latter downwards until the valve closes and the long steady stroke is repeated. Details of the valve assembly and the simple push-out water valves are shown enlarged at (*a*) and (*b*) respectively.

Owing to congestion of the mouth of the titration vessel by electrode-assemblies, etc., stirring by normal methods in potentiometric and similar

micro-titrations may be difficult. One useful method is to rotate the titration vessel. Where the volume of solution exceeds a few ml, too high a speed may cause loss by centrifugal action. A steady rate of

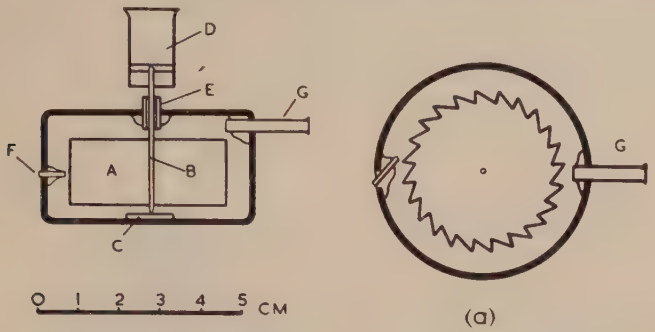



Abb. 6. Turbine-Type Suction-Operated Micro-Stirrer (*a*) plan view of rotor.

about 100 r. p. m. may be maintained by a *submerged-rotor turbine* driven from the water-tap[7]. For small samples, the simple *suction-operated turbine* shown in Fig. 6 is satisfactory[8]. Two large bakelite reagent-bottle caps placed mouth-to-mouth and joined with adhesive cellulose tape enclose cork rotor *A*. The latter has about 32 ratchet-shaped teeth as shown at (*a*), cut by means of a razor. Spindle *B* is a darning needle, the point of which runs on a small piece of microscope slide *C* and on the upper end of which is titration vessel holder *D*. Bearing *E* is a waxed-in short length of thick-walled glass tubing. Jet *F*, a 5-mm length of narrow melting-point capillary, and pump connection *G* are cemented into suitably-drilled holes as shown at (*a*).

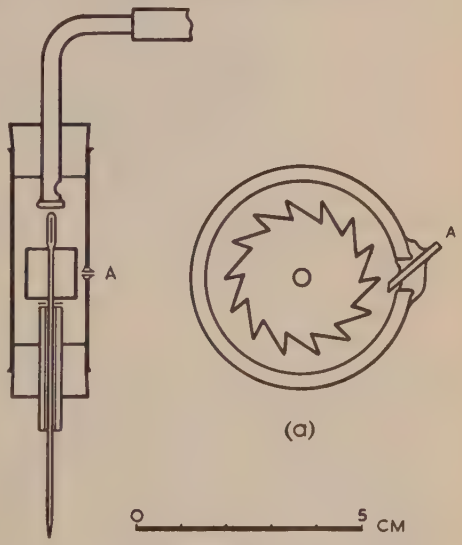
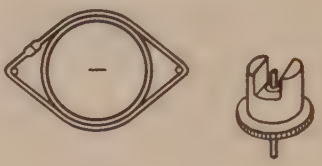



Abb. 7. Miniature Overhead Turbine-Type Stirrer (*a*) enlarged cross section.

Devices of this kind may be made much smaller and adapted for overhead stirring[7]. The rotor of the *miniature stirrer* shown in Fig. 7 is made by cutting teeth on an ordinary $^1/_2$″-headed taper cork. A jet is cemented into a hole in the jacket, as shown enlarged at (*a*). Inrush of air through the jet drives the rotor, while secondary air rising through the main bearing lifts the

rotor and spindle, causing the pointed end of the latter to bear upon the flat closed end of the pump connection. Running is therefore nearly frictionless and the degree of suction required is low.

Since agitation is greatest at the bottom of the vessel, magnetic bar stirring is both effective and splash-free[9,10]. The driving system of the *suction-operated magnetic stirrer* shown in Fig. 8 is identical with that of Fig. 7, but a powerful magnet in the form of a slotted $^1/_2''$-diameter cylinder* is mounted on the upper portion of the spindle[8]. The underside of the bakelite bottle cap forming the



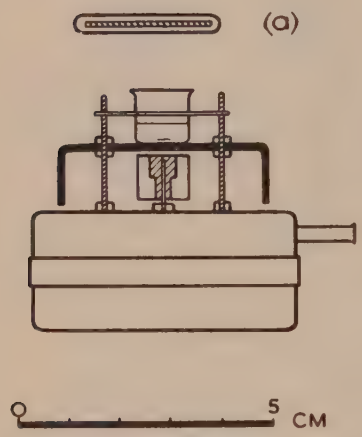



Abb. 8. Suction-Operated Magnetic Bar Stirrer (*a*) enlarged view of stirrer bar.

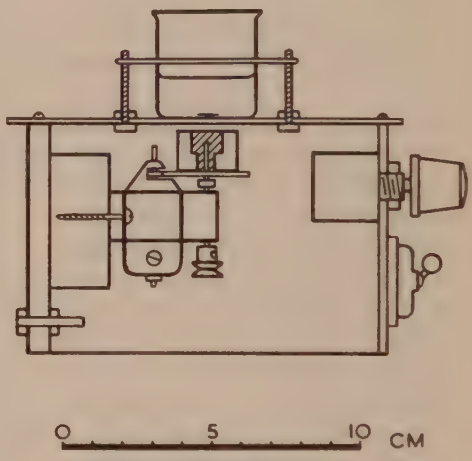



Fig. 9. Battery-Operated Magnetic Bar Stirrer.

titration platform clears the magnet by about 2 mm. Shown enlarged at (*a*) in Fig. 8, the stirrer bar consists of a few mm of sewing needle or two strands of fine iron wire sealed up in a piece of melting-point capillary.

Electric drive, provided by a small electric motor, may replace filter-pump operation. Whereas, however, bar-stirring is most effective with a magnet speed of a few hundred r. p. m. (above this the bar ceases to spin steadily), this speed is too low for certain starting and steady running of small motors. Use of a miniature geared motor** overcomes this difficulty; in the stirrer shown in Fig. 9, the magnet is merely cemented to the upper face of the final drive gear.

* James Neill (Sheffield) Ltd. Type M. 4776 A.

** Victory Industries, Ltd., Guildford. "Mighty Midget" pattern.

## II. Inorganic Qualitative Analysis.

Although only about 9″ long, the unit for semi-micro inorganic qualitative analysis[11] shown in Fig. 10 incorporates practically all apparatus needed for the separation and detection of the more usual radicals[12]. When not in use, the teat pipette is stored in a horizontal hole bored in one end of the block. Alongside in a second hole is a tube containing test papers. Some progress has been made with a scheme incorporating the less usual radicals[13].

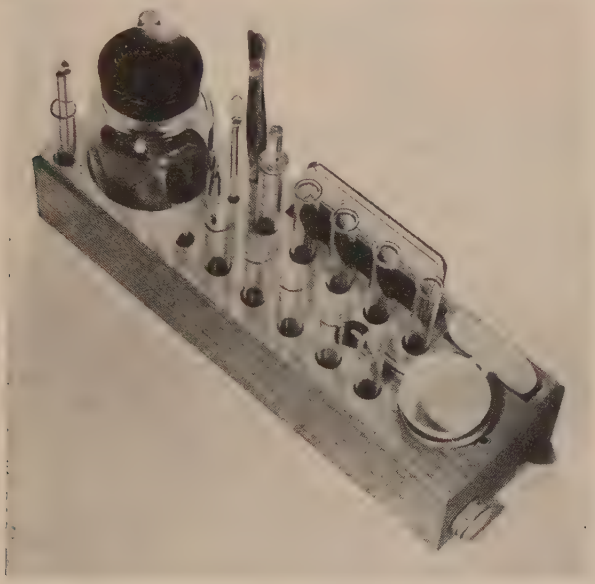


Fig. 10. Compact Unit for Semi-Micro Inorganic Qualitative Analysis.

The favourable surface-to-volume ratio in micro- and semi-micro analysis allows rapid saturation by merely agitating the solution in an atmosphere of hydrogen sulphide[14]. The gas is obtained either from a Kipp generator or from an even simpler low-pressure micro-generator[15]. More commonly, the gas is bubbled through the solution, using a delivery tube drawn down to a capillary outlet as at (*a*) in Fig. 11. Alternatively, the delivery attachment (*b*) may be used[16]. This is connected directly to the gas control tap and enables 0.3-mm bore parallel delivery tubes (which are easily pulled from scrap glass tubing and are cheap enough to be rejected after a single usage) to be employed. Over the 5-mm diameter hole in the adaptor wall is slipped a short length of tightly-fitting thin rubber tubing. The red-hot point of a needle is thrust through the

centre of the diaphragm thus produced. When required, a capillary is thrust into the tiny perforation, which is marked by a small cross or circle of white ink. With this device, accidental opening of the control tap does not produce the usual outrush of gas into the atmosphere.

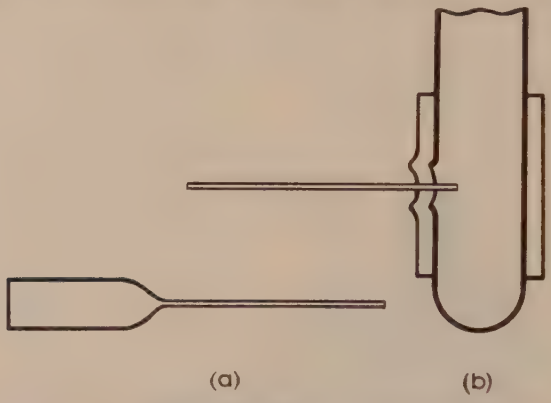



Fig. 11. Delivery Tubes for Hydrogen Sulphide (*a*) conventional form (*b*) plug-in type.

When using capillary delivery tubes, a gas pressure greater than that given by an ordinary Kipp generator is needed. The requisite pressure may be obtained by using a large head of acid[16,17], or from a pump system. An electric bell movement, the hammer of which strikes the thin rubber

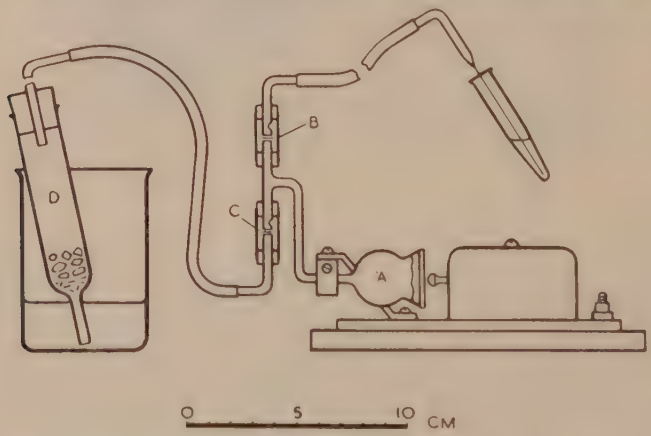



Fig. 12. Electrically-Operated Pump-Type Hydrogen Sulphide Generator.

diaphragm stretched over the mouth of funnel *A*, operates the pump-type generator shown in Fig. 12. Valves *B* and *C* are discs of thin sheet rubber and are cut with a corkborer[18]. Generation of gas in *D* cannot occur until the pump is started[19]. The general construction of the hand-operated

generator shown in Fig. 13 is self-evident[20]. The rubber disc valves are pressed lightly on their seatings by short lengths of glass rod *AA*. Gentle operation of the lower rubber teat *B* draws up the acid and causes generation of hydrogen sulphide. Further operation delivers the gas under a pressure high enough to allow a delivery orifice as small as 0.1 mm diameter to be used. The advantages are (*i*) the issuing bubbles are very small (*ii*) the maximum delivery is far below the rate of generation, so that acid cannot be drawn up into the pump and (*iii*) upper teat *C* has a reservoir effect giving continuous bubbling on compressing *B* two or three times per minute only. The alternative valve system shown at (*a*) is a recent development and does not stick when damp. Tube *D*, at the top of which is mounted the operating teat, has two pinholes *E* and *F*. Inlet valve *G* is a rolled-up rectangle of thin sheet rubber large enough to tightly close *E* by natural spring. Outlet valve *H* is of the same material and is retained by rubber tubing rings *II*. Considerable reservoir effect is provided by space *J*.

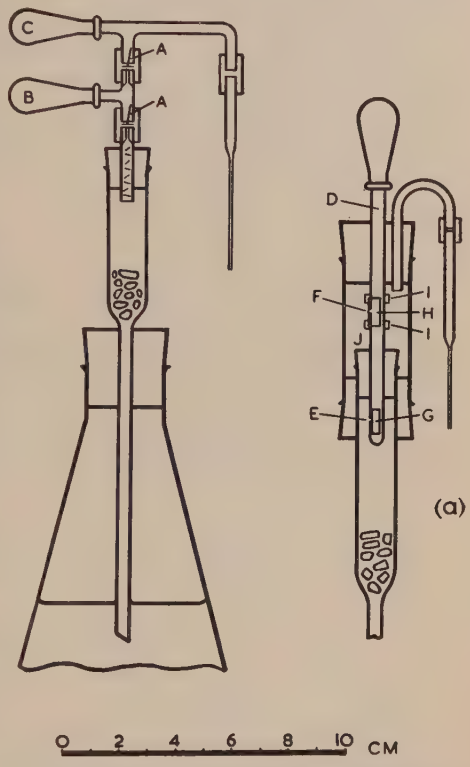



Fig. 13. Hand-Operated High-Pressure Hydrogen Sulphide Generator. (*a*) improved valve system.

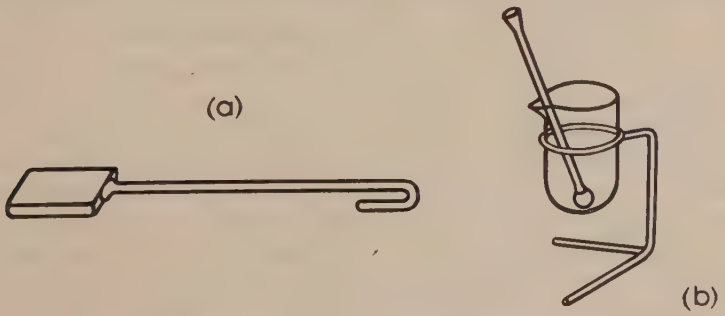



Fig. 14. (*a*) Micro Spot Plate, (*b*) miniature pestle and mortar.

Numerous other simple accessories[21], such as a micro test tube stand[22], devices for testing drops of liquid[1,23], and a stand for supporting microscope slides[24] may be constructed largely from glass rod. One form of micro spot-plate cut from scrap opal sheet glass is shown at (*a*) in Fig. 14. The hook-ended handle allows the device to be hung from the rim of a beaker and is of 3-mm diameter glass rod[25]. A piece of glass rod and the bottom of a thick-walled test tube are used to make the micro pestle and mortar shown at (*b*). Provided that the pestle is ground into the mortar before use, this simple device is very effective[18]. It may be supported in a large cork or a wire frame.

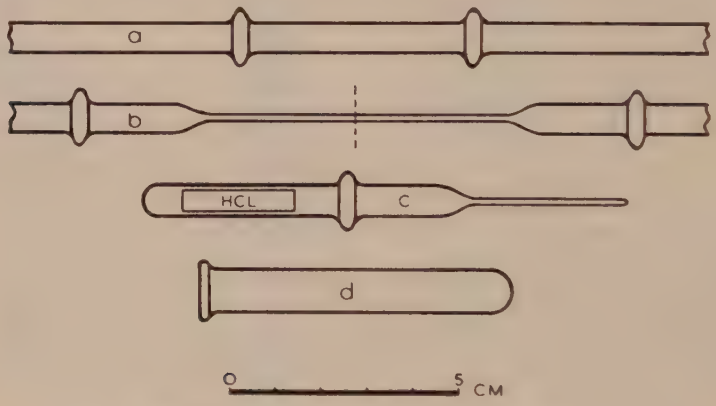



Fig. 15. Construction of Micro Reagent Bottles.

Although the consumption of reagents in microanalysis may be small, the number of items is usually at least as large as on the macro scale. Supplies of micro reagent bottles may be easily made from glass tubing as indicated in Fig. 15. Flanges about 7 cm from each end are formed on a 25-cm length of 5-mm bore glass tubing, as shown at (*a*). After drawing out as at (*b*), the narrow portion is cut to length. Attachment of rubber teats produces two stoppers with pipette-type dispensers. Labels are affixed and covered with transparent cellulose tape. Alternatively, rod-type dispensers may be made by removing the narrow portion completely and sealing on a length of fine glass rod. With this type of stopper, the label is rolled up and slipped inside the open end, when the latter is sealed as shown at (*c*). Rimmed containers (*d*) are made from 9-cm lengths of glass tubing in which the stoppers have a clearance not exceeding 1 mm. After assembly in pairs, the underside of each stopper flange is ground into the rim of the corresponding container. The finished bottles are mounted in a suitably-drilled wood block[26].

Constructed mainly from 2-mm bore glass tubing, the gas-testing device shown in Fig. 16 fits into the mouth of a micro test tube[27]. Test papers may be instantaneously inserted or withdrawn, gripping pressure being provided by the thin rubber band *A*. Gas escapes through the narrow annulus around the glass-rod guide-arm *B*. Devices for the preparation of fusion capsules from nickel foil[28] and a simple self-contained electric centrifuge for microgram-scale studies were also exhibited[29].

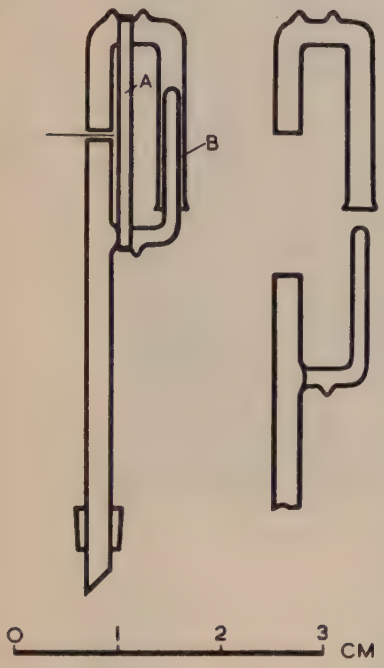



Fig. 16. Gas Testing Device.

### III. Organic Apparatus.

Although entire changeover to small-scale synthesis is neither practicable nor desirable, much may be gained by the introduction of such methods into first-year courses in organic chemistry[30]. 20-ml flasks and

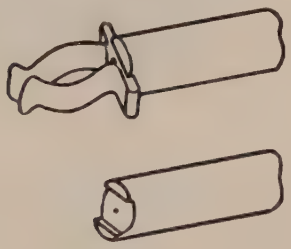


Fig. 17. Simple Spring Clamp.

other apparatus of corresponding size may be stored and issued in standard sets in partitioned boxes less than 12″ square and 3″ deep. Ordinary bossheads hold the spring clamps shown in Fig. 17. Use of such clamps greatly reduces breakage risk. The hardwood shanks are slotted at one end to suit a "Terry clip".

The double-sided unit shown in Fig. 18 includes small-scale apparatus assembled for most of the common operations of organic chemistry, such as simple, fractional, and vacuum distillation, continuous extraction, etc. Additional items (and thermometers during transport) are stored in a long drawer in the base. Designed for demonstrating small-scale techniques, the unit may prove useful for mobile laboratories, etc.

Sealed-tube reactions are conveniently performed in a heating device (Fig. 19) which is based upon a tin can filled with small nails[31]. Pockets

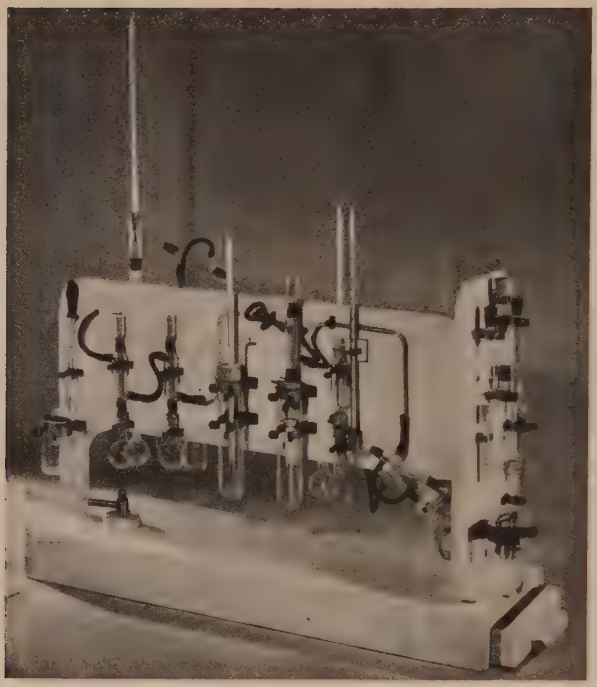


Fig. 18. An Organic Laboratory in Miniature.

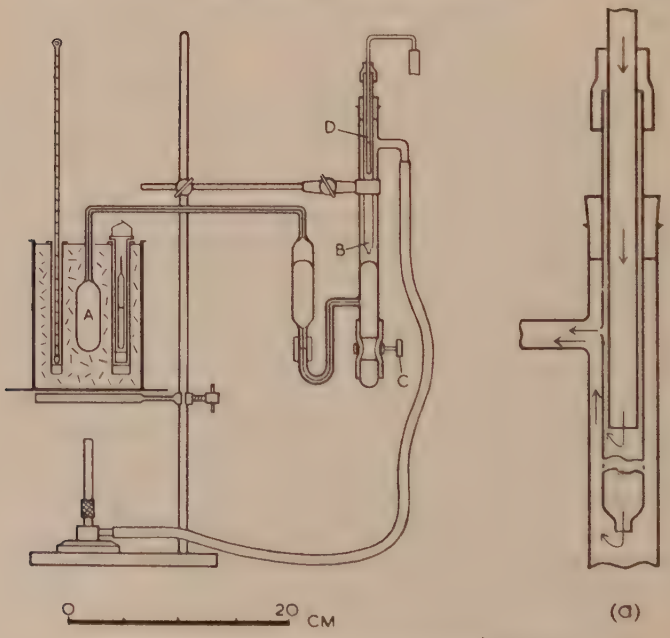



Fig. 19. Thermostatically-Controlled Heating Block.

for the thermometer and for reaction-tube holders are old corkborers which are tightly plugged at the lower ends with fine steel wool. Reaction tubes are placed in similarly-plugged corkborers which slide easily into the pockets and have lifting loops for easy handling. Expansion of air in bulb *A* cuts off that portion of the gas supply which passes through jet *B*. The temperature-setting, which is held to about $\pm 2°$ C, is adjusted by screwclip *C*. A variable byepass *D* [shown enlarged at (*a*)] is incorporated.

The audible signalling of softening or melting afforded by the device shown

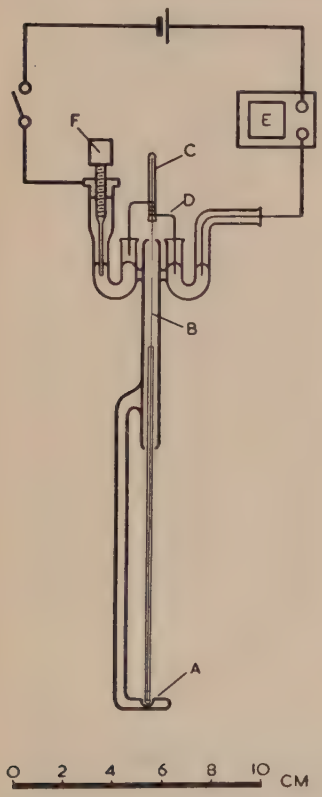



Fig. 20. Melting-Point Apparatus Giving Audible Indication.

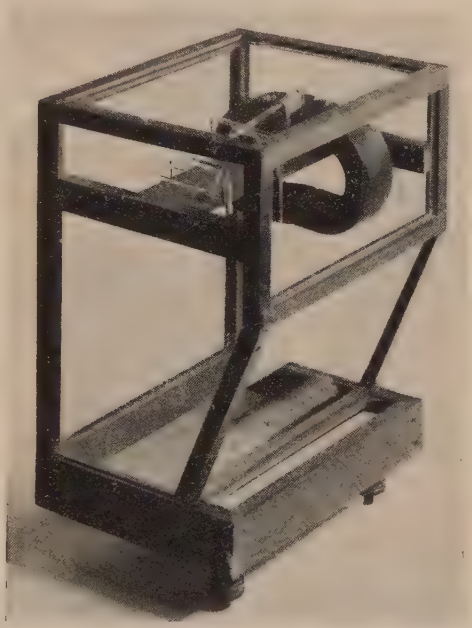


Fig. 21. Glass-Beam Direct-Reading Microbalance.

in Fig. 20 is useful when sharp liquefaction does not occur[32]. A depression in the foot of glass frame *A* supports the melting-point tube, down which passes fine glass rod *B*, resting on the sample. A light cap *C*, round which is twisted contact wire *D*, is supported on the upper end of the rod. As the latter sinks into the liquefying sample, the shorter leg of the contact wire touches the left-hand mercury surface, causing alarm *E* to sound. The stage at which this occurs depends upon the position of screw *F*, which controls the height of the mercury.

Two direct-reading glass-beam balances for small-scale preparative work have been developed. Oil-damping is used in one[33], the smaller version shown in Fig. 21 having heavy magnetic damping. Although accurate only to the nearest 0.25 mg, the smaller balance is almost "dead-beat". When in use, the top of the case is removed, exposing the beam assembly (Fig. 22). The centre portion *A* and pivot mounting *B*

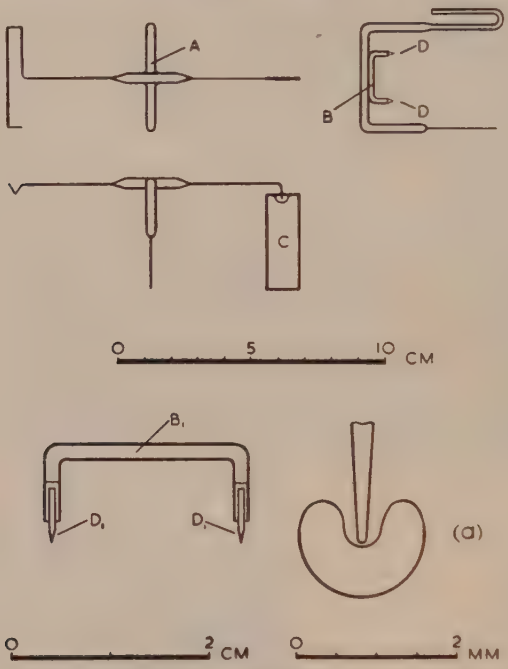



Fig. 22. Beam Assembly of Microbalance (*a*) pivot system.

are of thin-walled tubing; except for the aluminium foil damping vane *C*, the remainder is of fine glass rod[34]. Pivots *DD* are the pointed ends of fine needles and are cemented into *B*. The needle-points rest in a bearing trough which is shown in enlarged section at (*a*). A variety of sizes of such troughs may be made by blowing a hole in the wall of a length of tubing, heating in the region of the hole and pulling apart the ends of the tubing.

Fig. 23 illustrates an alarm to prevent over-distillation in Kjeldahl nitrogen determinations, etc.[35] A contains a bead of mercury and floats with about half its length immersed. Guide *B*, carrying two contacts [shown enlarged at (*a*)] slips easily into the stem of *A* and is attached to the condenser by rubber bands. Tubular support *C* is slightly constricted at the lower end and is slipped over the stem of *A* before the latter is

flared out. To set the device, the volume of liquid required to be collected is placed in the receiver and the indicator is slowly lowered until the mercury bead just short-circuits the contacts and causes the sounding of alarm *D*. Although simple, the device will reproduce a given depth to within a few mm.

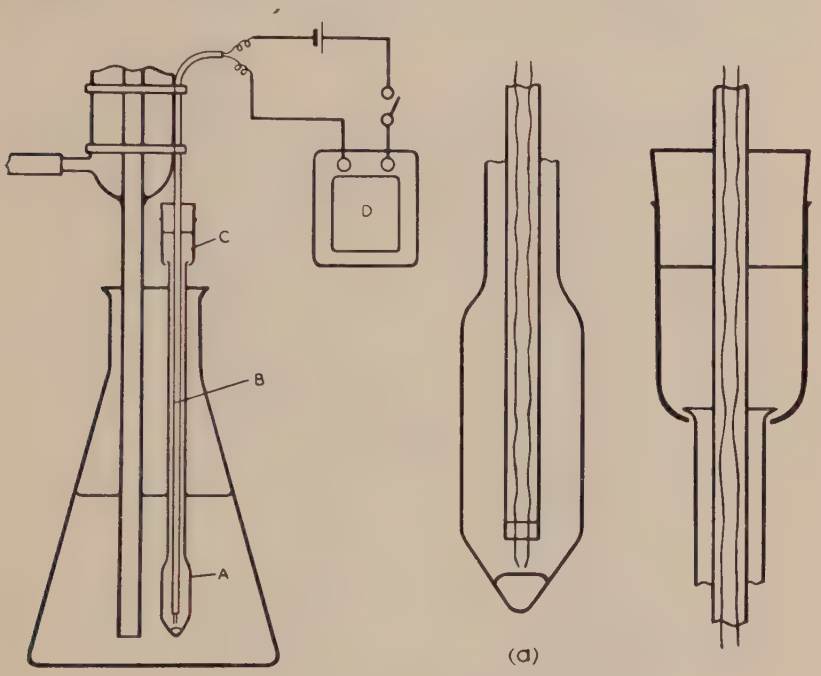



Fig. 23. Distillation Alarm (*a*) arrangement of contacts.

A micro-separatory device for solvent extraction[36], a froth-dispersal attachment for difficult refluxing operations[37] and a centring device for the introduction of sulphuric acid into Gerber tubes[38] were also available for inspection.

## IV. Electrochemical Techniques.

A compact polarising unit[39] for amperometric titration[40–48] giving variable galvanometer damping[49] and two cells suitable for amperometric titration and polarography[44,50–55] were exhibited. As shown in Fig. 24, the larger cell is constructed from a 1″-diameter boiling tube[56]. The 0.5-mm clearances in the T-pieces of the dropping mercury electrode[57] and of the jet of the microburette are ample for the entry and egress of the gas stream used for deoxygenation or mixing. During bubbling,

the solution is forced away from the dropping electrode, breaking the circuit and preventing galvanometer overload. More complex in construction, the smaller cell shown in Fig. 25 permits the titration of 1 ml or less of solution[58]. Solution-containers are interchangeable, so that repetition work is simplified[45–47]. The tangential arrangement of the gas inlet promotes mixing by causing the liquid to spin.

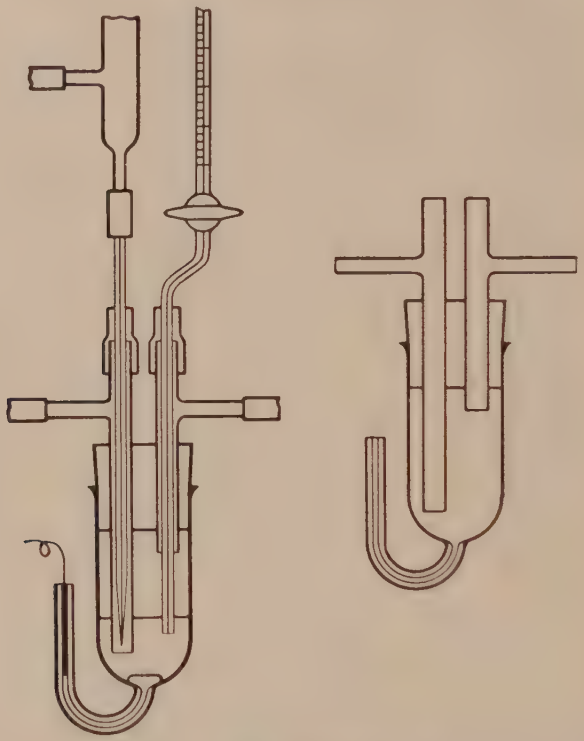


Fig. 24. Simple Polarographic Cell.

Constructed in about 15 minutes, the conductometric electrode system shown in Fig. 26 is suitable for either macro or micro work[59, 60]. A length of No. 24 S. W. G. platinum wire is thrust down a piece of melting-point tubing and sealed in at one end, so that about 10 mm of wire projects. This operation is repeated and the two tubes are secured side-by-side by sleeves of cycle valve tubing *AA*. Except for attachment of connecting leads, the fusing-on of glass bead *B* completes the assembly. Platinising takes about 2 minutes only. Examination of small depths of solution is made possible by bending the electrodes as shown in enlarged side view (*a*). Using a magnetic bar stirrer, the titration of samples

1 ml or less in volume is then possible. Left unplatinised, this electrode system may be used for the titration by the "dead-stop end-point" technique[61, 62].

A simple mains-operated titration unit gives good results with these

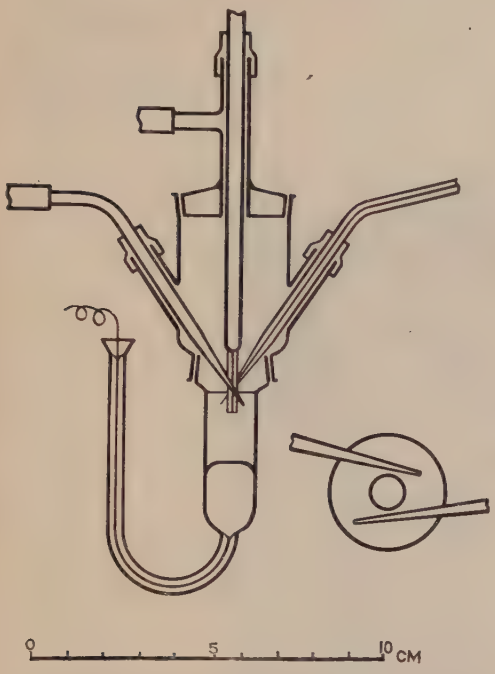



Fig. 25. Micro-Cell for Polarography and Amperometric Titration.

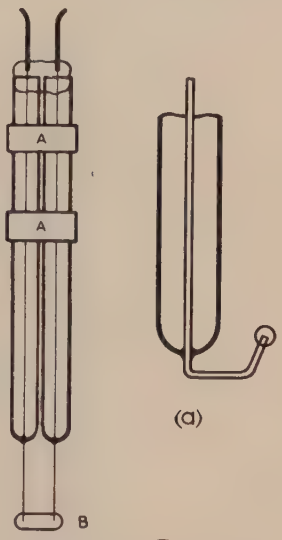



Fig. 26. Micro-Electrodes for Conductometric Titration. (*a*) enlarged side view after bending.

conductometric electrodes. Bell transformer *A* (Fig. 27) supplies about 3 volts to potentiometer *B*, which has a resistance of about 15 ohms and controls the *A*, *C* voltage applied to electrode terminals *C*. After

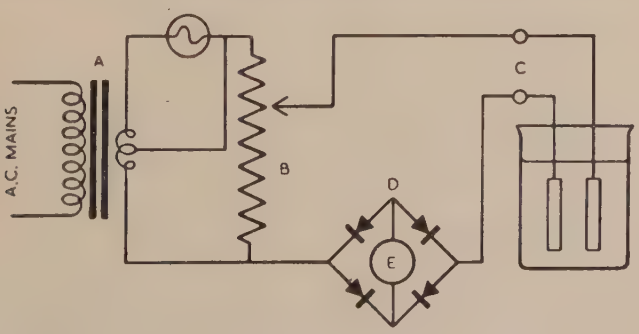



Fig. 27. Mains-Operated Conductivity Unit.

rectification by instrument rectifier $D$, the current passing through the solution is indicated by 0–1 milliampere meter $E$. This arrangement is useful for the titration of solutions of low to moderate conductivity (e. g., 0.001 N to 0.01 N hydrochloric acid) and for certain experiments in kinetics, etc.[63]

Electrical standardisation is provided in the direct-reading single-valve $p_H$ meter shown in Fig. 28[64]. Although conceived for use in teaching

Fig. 28. Direct-Reading pH Meter.

with the aid of large, low-resistance cell-systems, the meter operates quite satisfactorily with micro-potentiometric systems having tiny electrodes and quite high resistances[44, 65, 66]. It will not operate with a glass electrode.

A quinhydrone indicator electrode is used with this meter, a similar electrode in a $p_H$ 2.08 buffer acting as a reference. To operate, switches $S_1$ and $S_2$ are moved to the positions shown and the instrument is allowed to warm up. With switch $S_3$ in position 1, $R_7$ is used to bring the pointer of the re-scaled microammeter to a red line drawn at $p_H$ 8. $S_3$ is then

returned to its normal position 2 and knob $R_1$ is used to bring the pointer to another red line drawn at $p_H$ 2.08. Knobs $R_4$ and $R_1$ are now successively adjusted until the pointer swings to $p_H$ 8 as $S_3$ is moved to position 3 and returns to $p_H$ 2.08 when $S_3$ is returned to its normal position. Direct indication of an unknown $p_H$ is then obtained on moving switch $S_1$ to "*Read*".

## V. Volumetric Apparatus.

Using a slightly-modified oblique-way stopcock, the control of flow from a burette may be increased from the usual 10° of rotation to as

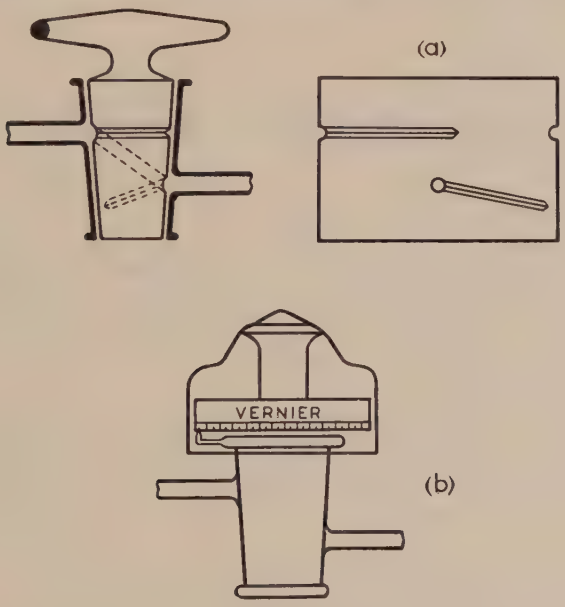



Fig. 29. Fine-Control Stopcock. (*a*) projection of plug surface, (*b*) wheel-type plug-head.

much as 150°[67]. Two file-grooves are cut on the surface of the plug, as shown in Fig. 29. One, from the upper end of the way, extends just over half way round; it is cut squarely, i. e., at right angles to the axis of the plug. Going in the opposite direction, the second groove starts at the lower end of the way, is cut obliquely, as shown in treble broken lines, and extends a little less than half way round. The plug surface is shown in projection at (*a*). Turned in one direction, the usual on-off action occurs; in the other direction, fine control is obtained. The drop-time may be easily varied between a few seconds and several minutes. The modified wheel-type plug head with a graduated scale as shown at (*b*) is useful for the general fine control of gas or liquid flow.

Several forms of top-control microburette have been developed[68, 69], including the cam-controlled version[70] shown in Fig. 30. The flow is controlled by rotating the knob, as shown at (*a*) and (*b*). This operates a lateral cam (made from two telescoping corkborers) which presses rubber-faced glass plunger *A* on to the squarely-ground end of burette-stem *B*. The latter is held in place by a snugly-fitting sleeve *C* of rubber tubing and is easily interchanged. Originally designed for 1-mm bore

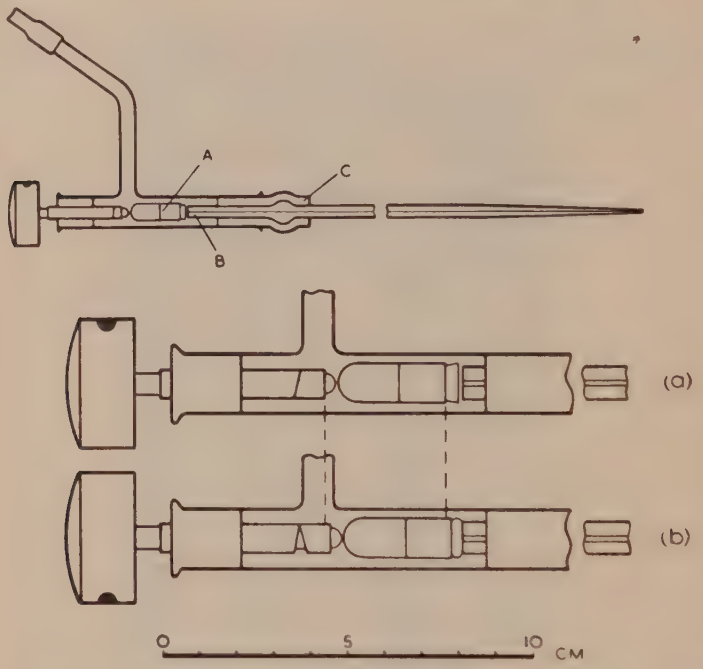



Fig. 30. Cam-Controlled Microburette. (*a*) valve open, (*b*) valve closed.

burette stems mounted in a clamp-on scale unit[68]. the control-head allows a 1-ml graduated pipette to be used as a microburette. Even larger pipettes may be used if their upper ends are reduced to fit into the head. Also exhibited were a syringe pipette[71] and a microburette which delivers by compression of a rubber sac[70].

Intended for delivering reproducible drops of solution to a microscope slide, the device shown in Fig. 31 proved useful for spotting test papers[72]. The spots produced are uniform to within about 10%. Container *A* is about 1.5 mm bore at the tip. After grinding in the drawn-down end of plunger *B*, the lower end of the latter is cut to project not more than 1 mm. The extent of projection, which must be at least 0.3 mm for spotting papers, controls the delivery. Holding the device vertically

with the forefinger resting lightly on the plunger head, the tip is brought down sharply and squarely on the slide or paper. Reproducible spotting at about one per second is simple after a little practice.

Provided that it is kept grease-free, the dispenser shown in Fig. 32 allows quantities of about 1 $\mu$l of liquid to be measured on to microscope slides, etc.[73] Spheres about 1.5 mm in diameter are formed on the ends of two 0.7-mm diameter glass

Fig. 31. Device for Spotting Test Papers.

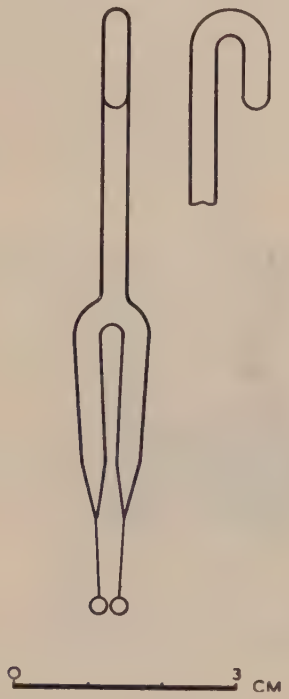



Fig. 32. Device for Dispensing Microlitre Quantities.

threads. With the spheres alongside and about 0.5 mm apart, the free ends of the threads are fused together and attached to a glass handle. In use, the device is held vertically and lowered until it just touches the liquid surface. The drop, which is picked up between the spheres (Fig. 33), is delivered by touching the microscope slide with both spheres at once.

In connection with a device for following the washing of gravimetric precipitates[74], an unusual requirement was the reproducible delivery of small quantities of boiling wash solution. The modified wash-bottle shown in Fig. 34 made this possible[75]. Inner vessel *A* has a sealed-in syphon tube *B* and carries a wash-bottle fitting. Delivery tube *C* is of 1.5-mm bore tubing, *D* being a length of cycle-valve rubber tubing.

The whole unit is mounted in a flask, the stopper of which carries a vent tube *E*. When the liquid is boiling, *E* is closed by a rubber-clad finger until the level in *A* has risen above the upper end of *B*. The bottle is removed from the hotplate, the excess liquid allowed to syphon back into the flask, and the contents of *A*, which are kept hot by vapour jacketing, are at once blown out, *E* being closed again meanwhile. Volumes of between 0.5 and 5 ml may be delivered with a reproducibility of 0.05 ml or better. The volume delivered is adjusted by sliding delivery tube *C* in its stopper. When operating below the boiling point, *A* is filled by blowing at the vent tube.

Fig. 33. Drop Suspended on Dispensing Device.

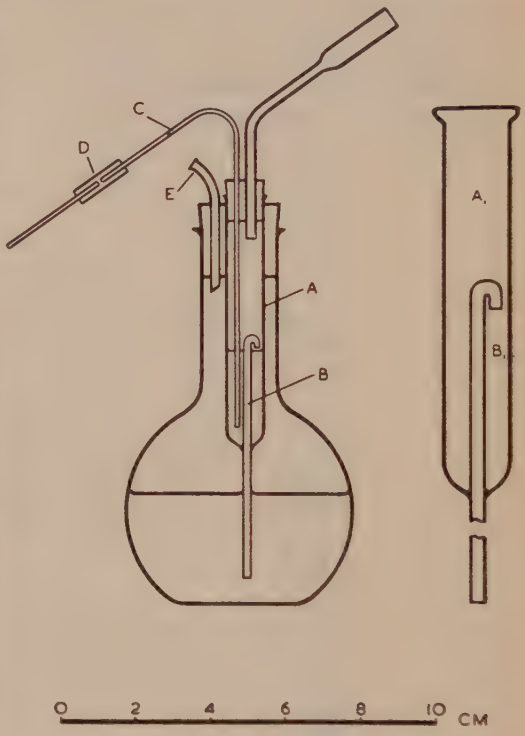



Fig. 34. Device for Metering Boiling Water.

## VI. Miscellaneous Devices.

Designed for the continuous indication or recording of pressure-changes during oxidation studies, the transmitting manometer shown in Fig. 35 may be placed in an air thermostat alongside the apparatus to which it is sealed[76]. Fine platinum filaments *AA* pass centrally down the limbs and constitute a Wheatstone network with small resistances *B* and *C*. The unbalance of the network operates recorder *D*, which, with the controls, is of course outside the thermostat. Pressure-changes

displace the mercury, altering the effective lengths of the filaments and hence the state of unbalance.

The continuous recording of unbalance has also been applied successfully to molecular-weight studies, using a thermistor in a Cottrell-type ebulliometer developed from a simpler version designed for teaching purposes[77]. The modified apparatus has been used to study the kinetics of the catalysed self-addition of acetone at the boiling point[78]. A simple and rapid semi-micro Victor Meyer-type vapour density apparatus has also been developed[79].

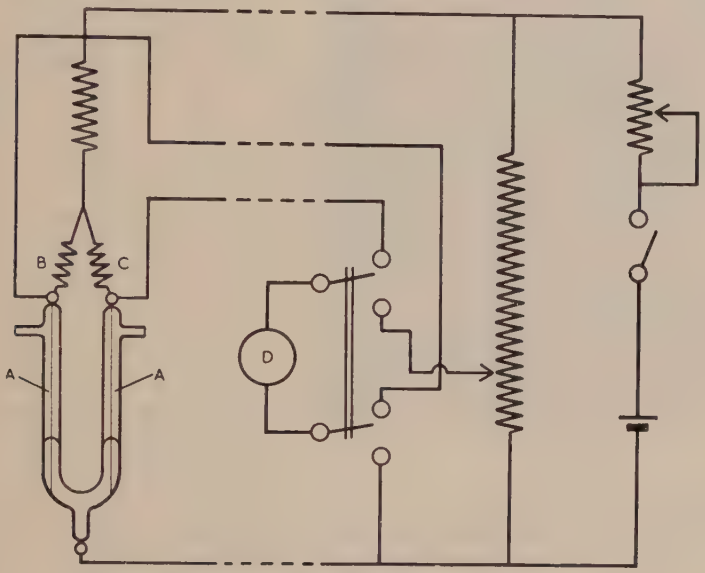



Fig. 35. Electrically-Operated Transmitting Manometer.

Using cooling by evaporation of ether in an air-stream controlled by a mercury regulator, the constant temperature of a cold thermostat bath may be conveniently maintained[80]. Where precise control is not required, a simple gas thermoregulator made from a broken pipette is useful[81].

Apart from the reservoir *A*, the float system, and the covering clock-glass, standard ground-jointed parts are used in the apparatus (shown in Fig. 36) for the continuous production of double-distilled water. A rapid stream of distilled water from a steam oven, etc., maintains a constant level in *A*, the overflow being suitably collected. A platinum wire hook-and-eye *B* unites the two floats, the buoyancy of the system being adjusted so that although valve *C* remains closed when the immersion of the lower float is about 5 mm, it opens if the level in the flask falls[82].

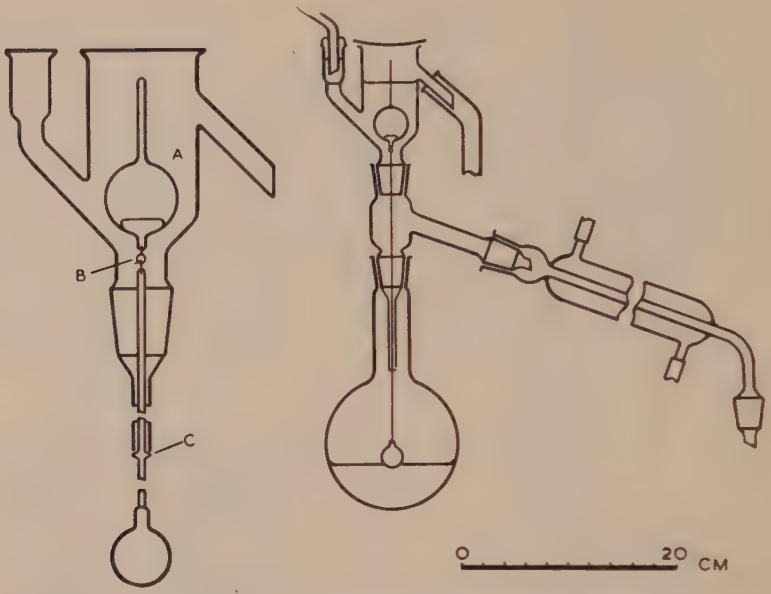



Fig. 36. Apparatus for Production of Double-Distilled Water.

The micro-blowpipe shown in Fig. 37 is useful for construction of apparatus from melting-point tubing and fine glass rod[83]. Gas chamber *A* is an $1^1/_2$″-outside diameter steel washer, on the faces of which are soldered discs of copper foil. A sewing needle is driven squarely through both discs, as shown at (*a*), so that the point emerges by about 1 mm. The smaller hole is the air jet, the flame issuing from the larger one. Gas enters the chamber through hole *B*. Attachment of connections *C* and *D* completes the assembly. Air-pressure is supplied by a suction-operated pump which is similar to but larger than the stirrer shown in Fig. 2 and which carries on its lower side tube a valve chest similar to that shown in Fig. 6. Operating at about 200 strokes per minute, this pump gives a steady flame if a reservoir (e. g., a 2-litre flask) is placed in the delivery line to the blowpipe.

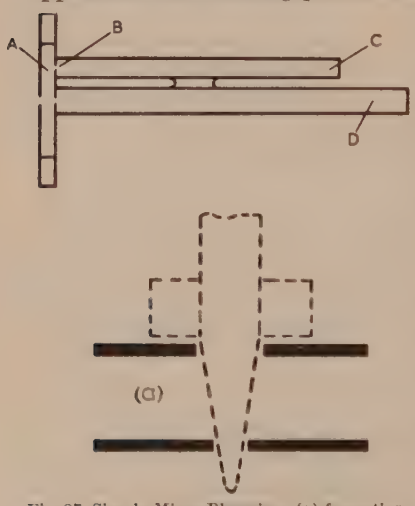



Fig. 37. Simple Micro-Blowpipe. (*a*) formation of gas and air jets.

Numerous supporting and clamping devices, constructed largely from bakelite bottle-caps, were exhibited[24]. A rise-and-fall motion, operated by two small rubber rollers which grip the sides of the glass rod "hairpin", is incorporated in the two devices shown in Fig. 38. The stand on the right has a turbine-type suction stirrer, similar in internal construction to that shown in Fig. 8, which may be lowered into a solution by rotation of a knob on the head. Carried on the head of the stand on the left is a horizontal socket for the attachment of accessories such as a Belcher micro-spoon or the glass clamp shown in Fig. 39. Constructed from 3-mm diameter rod, the gripping force, provided by a band cut from rubber tubing, may be released by one hand[84]. These clamps may also be used in a universal mounting[85].

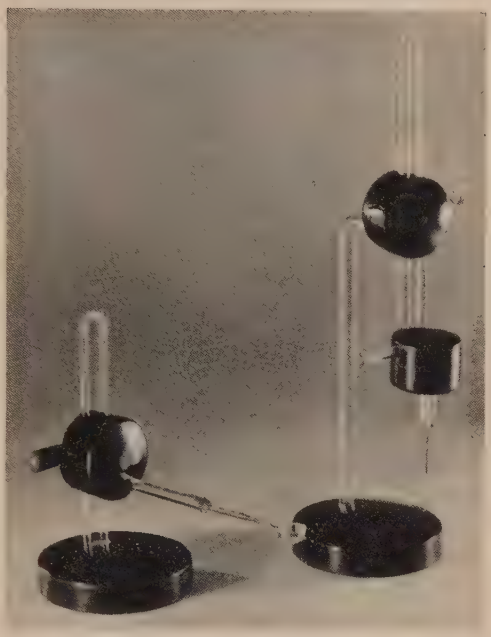


Fig. 38. Use of Bakelite Bottle-Caps in the Construction of Apparatus.

Weighing by the method of swings is facilitated by the accessory shown in Fig. 40. This allows the oscillation of the balance-beam to be

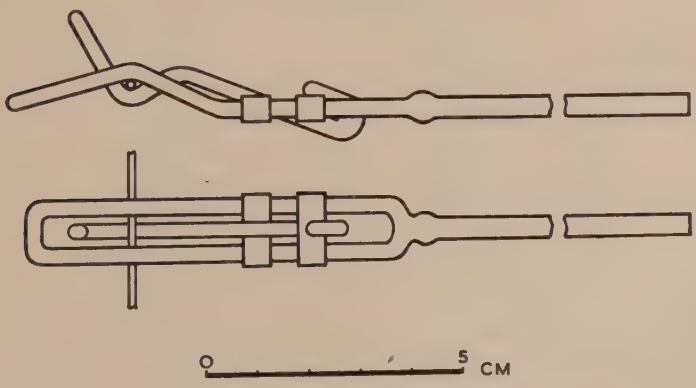



Fig. 39. Simple Glass Spring Clamp.

adjusted to any desired amplitude. The jet at the free end of the glass tubing frame points vertically downwards about 1 cm inwards from the

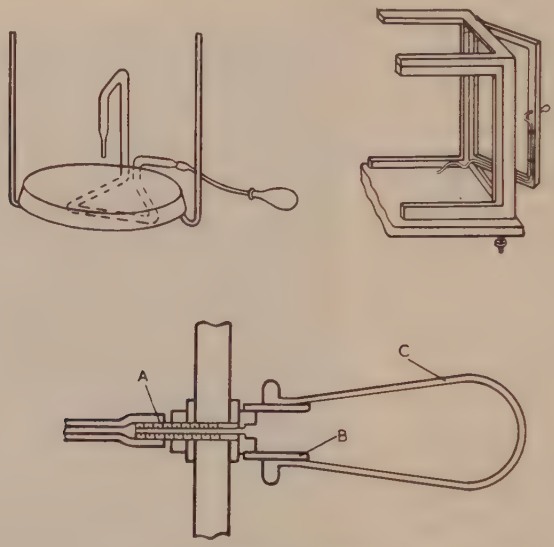



Fig. 40. Device for Adjusting Amplitude of Balance Swing.

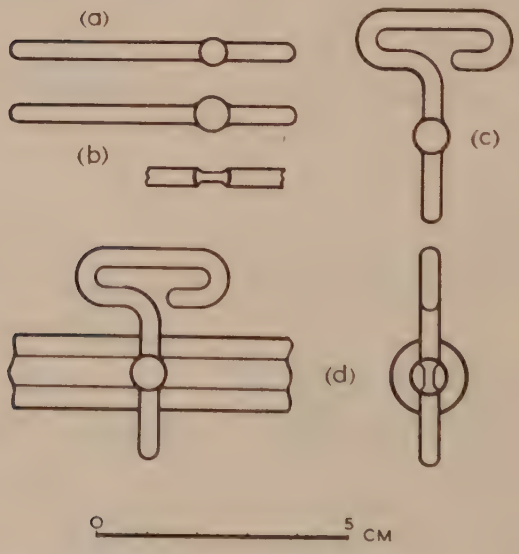



Fig. 41. Stages in Construction of Rubber-Bodied Stopcock.
(*a*) formation of ball, (*b*) formation of disc, (*c*) completed plug, (*d*) sections of assembled stopcock.

edge of the right-hand pan. Normally stored within the case, the rubber teat is placed on the bench when the balance is to be used, the sash being lowered gently so that the cycle valve tubing is not completely flattened. Light puffs of air enable the oscillations to be built up; a swing that is initially too large is easily reduced by sharp pressure on the teat as the pan *approaches* the jet[86]. For constant use, the catch of the right-hand door may be replaced by a longitudinally-drilled bolt *A*, to the head of which is soldered a short brass sleeve *B* carrying rubber teat *C*. The connecting tubing is then carried round the door frame under small cork bridges.

A wartime improvisation which has subsequently proved useful is the construction of stopcocks from rubber pressure tubing and glass rod[87]. To construct the plug from 5-mm diameter glass rod, a sphere is formed as shown at (*a*) in Fig. 41. Whilst still hot, the sphere is flattened into a round-edged disc about 10 mm in diameter and 3 mm thick as at (*b*). The plug is completed by bending up the handle, as shown at (*c*). Having bored a clean 4-mm diameter hole *right through* a piece of 4-mm bore pressure tubing, the latter is impregnated with vaseline. To assemble, the lightly-vaselined plug is merely forced into position, as shown at (*d*). Flow occurs between the parallel sides of the disc and the walls of the tubing, which do not collapse under vacuum. Rotated through 90°, the disc completely closes the way. Various modifications are of course possible. Other improvisations are glass-to-glass detachable joints made from heavy-walled tubing[88] and a simple suction-operated emulsifier[29].

## Summary.

About 70 pieces of microchemical and general apparatus developed during the past 10 years are described. The apparatus is classified in 6 sections, viz. stirring and allied devices, equipment for inorganic qualitative analysis, organic apparatus, electrochemical techniques, volumetric apparatus, and miscellaneous devices.

## Zusammenfassung.

Es werden etwa 70 mikrochemische und andere Apparate beschrieben, die in den vergangenen 10 Jahren entwickelt wurden. Es handelt sich hierbei um Geräte zum Rühren u. dgl., Einrichtungen für die anorganische qualitative Analyse, Apparate für organische Zwecke, für elektrochemische und volumetrische Verfahren und für verschiedene andere Bedürfnisse.

**Résumé.**

On décrit environ 70 articles relatifs à l'appareillage microchimique et général mis au point pendant les 10 dernières années. L'appareillage est classé en 6 sections, c'est-à-dire, dispositifs pour l'agitation et ce qui s'y rapporte, pour l'analyse qualitative minérale, l'appareillage organique, les techniques électrochimiques, l'appareillage pour volumétrie et des dispositifs variés.

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# Beitrag zur mikroanalytischen Filtrationstechnik.

Von

**Gerald Kainz.**

Mit 3 Abbildungen.

*(Eingelangt am 22. April 1953.)*

Vergleicht man den Zeitbedarf verschiedener chemisch-analytischer Arbeitsgänge miteinander, so zeigt sich, daß Filtrationen verhältnismäßig viel Zeit beanspruchen. Es schien daher vom praktischen Standpunkt aus wünschenswert, diesen oftmals durchzuführenden Arbeitsgang im Hinblick auf Zeitersparnis näher zu untersuchen.

Der Zeitbedarf bei mikroanalytischen Filtrationen ist hauptsächlich von zwei Faktoren abhängig: von der Durchlässigkeit der Filterschicht und von der Beschaffenheit des abzutrennenden Niederschlages. Über die Durchlässigkeit der analytisch verwendeten Filter — meist werden Filter aus Glas- oder Porzellansinter verwendet — orientiert Abb. 1*.

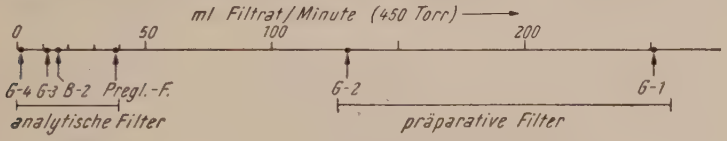


Abb. 1.

Im Hinblick auf die Filtrationsgeschwindigkeit scheint es also zweckmäßig, bei Mikro-Filtergeräten aus Porzellan (z. B. Filterstäbchen nach *Emich*) die Fritte B 2, bei Geräten aus Glas (z. B. Filterröhrchen nach *Pregl*) die Fritte G 1 mit Asbestauflage heranzuziehen. Außerdem empfiehlt es sich, gelegentlich die Durchlässigkeit der Filter zu überprüfen und zu wenig durchlässige Filter auszuscheiden.

* Außerdem werden auch Filter aus Platin-Iridium (nach *Neubauer*) hergestellt, die jedoch wesentlich teurer sind. Zum Überblick über die einzelnen Mikro-Filtriergeräte vgl. *Hecht-Donau*[1]. Bezüglich Bezeichnungsweise und Porendurchmesser von Glasfritten vgl. *Wittenberger*[2], bez. Porzellanfritten vgl. z. B. *Simon*[3].

Ein weiterer wichtiger Faktor für die Filtrationsdauer ist die Beschaffenheit des abzutrennenden Niederschlages. Je nach der Durchlässigkeit der am Filter zurückbleibenden Niederschlagsschicht sinkt die anfängliche Filtrationsgeschwindigkeit mehr oder minder stark ab. Besonders nachteilig äußert sich dieser Umstand dann, wenn man ein

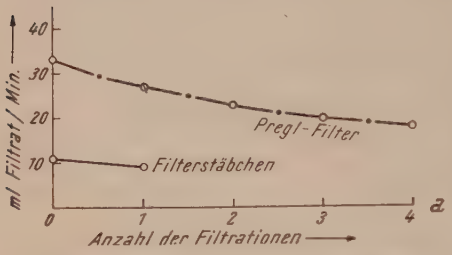


Abb. 2a. AgCl, aufgekocht; 4 mg Niederschlag pro Filtration.

Abb. 2b. Aluminiumhydroxyd; 4 mg Niederschlag pro Filtration.

Filter zwecks Zeitersparnis nicht nur für eine, sondern für möglichst viele Filtrationen, z. B. bei Serienbestimmungen, heranziehen will. Abb. 2 zeigt das verschiedene Verhalten eines grobkörnigen und eines gallertartigen Niederschlags auf einem Glasfritte-Asbestfilter bei mehreren aufeinanderfolgenden Filtrationen (bei 2b: rasche Verlegung des Filters).

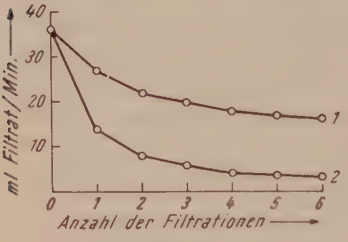


Abb. 3.
*1* Mit Vorfilter (Seesand),
*2* ohne Vorfilter.
Niederschlag: Aluminiumhydroxyd.

Experimentell zeigte sich nun, daß man diese starke Filtrationshemmung weitgehend ausschalten kann, wenn man vor der eigentlichen (sehr engporigen) Filterschicht eine weitporige, leicht auswechselbare Vorfilterschicht anbringt. Das Vorfilter, das schnell herstellbar sein muß, fängt den Hauptanteil des Niederschlages auf und wird, wenn erschöpft, ausgewechselt. Die eigentliche Filterschicht (z. B. Asbestschicht), deren Herstellung erfahrungsgemäß wesentlich mehr Zeit und Übung erfordert, dient nur zur Feinfiltration und bleibt somit für etwa 10 bis 15 Filtrationen intakt. Der dadurch erzielte Zeitgewinn ist, wie aus Abb. 3 hervorgeht, insbesondere bei Serienbestimmungen, beträchtlich.

Analytisch anwendbar sind diese Filter bei solchen Filtrationen, bei denen man *nicht den Niederschlag*, sondern das *Filtrat* zur weiteren Verarbeitung und Bestimmung benötigt*.

* Diese Fälle sind insbesondere durch die zunehmende Verwendung volumetrischer und kolorimetrischer Methoden zahlreich. Als Beispiele aus der organischen Mikroanalyse seien erwähnt: Herstellung von optisch klaren

Entsprechend dieser Anordnung bewährten sich folgende Filter:

1. *Seesand als Vorfilter und Asbest als Feinfilter.* Die Seesandschicht wird nach etwa zwei Bestimmungen ausgewechselt, die schwieriger herstellbare Asbestschicht bleibt für etwa zehn Filtrationen verwendbar.

2. *Watte als Vorfilter und Zellulosepulver als Feinfilter.* Wie sich zeigte, ist Zellulosepulvér, das sonst nur zur Verteilungschromatographie verwendet wird, auch ein ausgezeichnetes Material für Feinfilter. Die Herstellung eines solchen Filters ist sehr einfach. Außerdem kann man seine Durchlässigkeit dem abzutrennenden Niederschlag anpassen, wenn man das Zellulosepulver in mehrere Korngrößen aussiebt.

In analytischer Hinsicht ist noch folgendes zu bemerken: Trotz der größeren Filterschicht benötigt man zum quantitativen Auswaschen des Filters nicht wesentlich mehr Waschflüssigkeit als üblich. Beim Zellulosefilter muß — zum Unterschied vom chemisch indifferenten Seesand-Asbestfilter — berücksichtigt werden, daß das Filtermaterial, ähnlich wie Papierfilter[7], Carboxylgruppen (etwa 0,03 bis 0,3%) enthält. Es kann daher unter gewissen Bedingungen kationenaustauschend auf das Filtrat einwirken. So werden beispielsweise aus neutralen Lösungen verschiedene Kationen, wie Ag-, Cu-, Ni-, Mn- und Fe-Ionen in ganz geringer Menge zurückgehalten. Dies läßt sich jedoch vermeiden, wenn man in *saurer* Lösung filtriert.

Die beschriebenen Filter werden bereits seit längerer Zeit mit Erfolg für quantitative organische Mikrobestimmungen verwendet.

## Experimenteller Teil.

*Zur Messung der Filtrationsgeschwindigkeit:* Die Filtrationsgeschwindigkeit wurde mit einer Apparatur bestimmt, die aus Filtriergerät, Absaugeprouvette mit Maßeinteilung, Manometer[8] und Vakuumregulierflasche[9] bestand. Der bei der Filtration angewendete Unterdruck war so bemessen, daß die aus dem Filtriergerät austretenden Tropfen nicht verspritzten. Die in Abb. 1 verzeichneten Durchsatzgeschwindigkeiten der einzelnen Filter wurden mit Wasser, das vorher mehrmals filtriert worden war (vgl. *Simon*[3], *Hüttig*[10]), festgestellt (Durchschnittswerte). Mit derselben Anordnung wurden auch die Filtriergeschwindigkeiten der Abb. 2 und 3 gemessen.

*Herstellung eines Filters aus Zellulosepulver-Watte:* Zellulosepulver, das von Schleicher & Schüll sowie Whatman unter der Bezeichnung „Zur Verteilungschromatographie" in den Handel kommt, wird mittels eines Siebsatzes DIN 1171 in verschiedene Korngrößen ausgesiebt. Pro Filter benötigt man zirka 0,2 g des Pulvers, das man mit einem Maßlöffel abmißt, sodann

Lösungen für kolorimetrische Bestimmungen; Abtrennung von Kohleteilchen und gegebenenfalls Kieselsäure nach Peroxydaufschluß vor der gravimetrischen Bestimmung von Halogenen, Phosphor und Selen (vgl. Übersicht bei *Wurzschmitt*[4]); Abtrennung von Kohleteilchen nach Kaliumaufschluß vor der jodometrischen Titration von Jod und Brom (vgl. [5]); Abtrennung von Kohleteilchen und gefälltem Silberhalogenid vor der Titration von Chlor nach Kalium-, bzw. Peroxydaufschluß (vgl. [6]).

in Wasser aufschlämmt und mittels eines Heberrohres in ein *Pregl*sches Filterröhrchen übersaugt. Oberhalb dieser Filterschicht bringt man einen mit Wasser angefeuchteten, stark zusammengepreßten Wattebausch an. Die Watte soll nicht auf der Zelluloseschicht aufliegen. Der Wattebausch, der die Hauptmenge des Niederschlags aufnimmt, wird nach jeder Filtration erneuert; das Zellulosefilter ist unverändert für etwa 10 Filtrationen verwendbar.

*Herstellung eines Filters aus Seesand-Asbest:* Nachdem man auf die Sinterplatte eines *Pregl*schen Filterröhrchens in üblicher Weise eine Asbestschicht aufgebracht hat, schlämmt man feinen Seesand in Wasser auf und saugt ihn mittels eines Heberrohres auf das Filter (Schichtdicke 15 bis 20 mm). Wenn die Seesandschicht nach einigen Filtrationen erschöpft ist, wird sie mit Wasser aus dem Filterröhrchen herausgespült und erneuert. Das Asbestfilter bleibt hingegen etwa für zehn Filtrationen intakt.

## Zusammenfassung.

Zur schnellen Filtration, insbesondere bei Serienuntersuchungen des Filtrates, hat sich ein Mikrofilter bewährt, das aus zwei verschiedenen Filterschichten besteht. Die eine Schicht dient als Vorfilter, die andere als Feinfilter. Da das leicht auswechselbare Vorfilter den Hauptteil des Niederschlages aufnimmt, bleibt das eigentliche Feinfilter für viele Filtrationen intakt. Als Feinfilter bewährte sich sehr gut eine Schicht aus Zellulosepulver, als Vorfilter Watte. Beide Filterschichten befinden sich in einem Filterröhrchen nach *Pregl*. Als gut brauchbar erwies sich auch die Beschickung mit Asbest als Feinfilter und Seesand als Vorfilter.

## Summary.

A micro filter, which consists of two different filter layers has been found excellent for rapid filtration, particularly in series determinations in the filtrate. One layer serves as pre-filter, the other as fine filter. Since the lighter more readily exchanged pre-filter takes up the main portion of the precipitate, the actual fine filter remains intact after many filtrations. A layer of cellulose powder makes an excellent fine filter; cotton wool is good for the pre-filter. Both filter layers are housed in a *Pregl* filter tube. It has also been found that good results are secured by using asbestos as fine filter and sea sand as pre-filter.

## Résumé.

Pour la filtration rapide, particulièrement pour les dosages en série dans le filtrat, on a essayé un microfiltre formé de deux couches filtrantes différentes. L'une d'elles sert de pré-filtre; l'autre de filtre fin. Du fait que le pré-filtre, facilement interchangeable, retient la plus grande partie du précipité, le filtre fin proprement dit reste intact. Pour le confectionner, on utilise au mieux une couche de poudre de cellulose et pour l'autre de l'ouate. Les deux couches filtrantes sont logées dans un petit tube filtrant de *Pregl*. On recommande aussi la confection du filtre fin en amiante et celle du pré-filtre en sable de mer.

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# Über eine neue Methode zur Bestimmung des Germaniums.

Von

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*(Eingelangt am 9. April 1953.)*

## Einleitung.

Über die in komplexchemischer Hinsicht zwischen Bor und Germanium bestehende Verwandtschaft hat schon vor längerer Zeit *N. S. Poluektoff*[1] berichtet. So kennt man von der Germaniumsäure der Borsäure analoge, anionische Komplexe mit Di- und Polyolen, die zum Nachweis und zur Bestimmung des Germaniums herangezogen worden sind[2].

Nun haben *J. A. Gautier* und *P. Pignard*[3] in den letzten Jahren eine neue Methode zur semimikrogravimetrischen (und maßanalytischen) Bestimmung des Bors ausgearbeitet, die auf der Schwerlöslichkeit eines Bariumborotartrat-Komplexes basiert. Die Verbindung hat die analytisch ermittelte Zusammensetzung[4] $Ba_5B_2C_{16}H_{16}O_{28} \cdot 2\,H_2O$. Nähere Angaben über ihre Struktur sind noch nicht gemacht worden.

Bei der Erprobung dieser eleganten und schnellen Methode wurde vermutet, daß das Germanium zu ähnlicher Komplexbildung befähigt sein könnte. Diese Auffassung ließ sich in der Tat bestätigen. Im folgenden soll die Darstellung des Barium-Germanium-Tartrats beschrieben und über dessen analytische Verwendbarkeit berichtet werden.

## Die Bestimmung des Germaniums als Barium-Germanium-Tartrat.

### *1. Bildungsweise und Zusammensetzung der neuen Komplexverbindung.*

Versetzt man eine Alkaligermanatlösung in der Kälte mit der von *Gautier* und *Pignard* angegebenen Reagenslösung (das ist eine ammoniakalische Lösung von Bariumtartrat in Gegenwart von Ammoniumchlorid), so fällt ein weißer, flockiger Niederschlag aus. Die Analyse des bei 110° zum konstanten Gewicht getrockneten Reaktionsproduktes ergab als Mittel aus mehreren Bestimmungen die Zusammensetzung $Ba_2GeC_8H_{12}O_{16}$.

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Hierbei wurden das Barium wie üblich als Sulfat, das Germanium nach der Tanninmethode[5], Kohlenstoff und Wasserstoff durch Mikroelementaranalyse festgelegt.

Wie auch beim Bariumborotartrat bereitet die Bestimmung des Wassergehalts der Barium-Germanium-Tartrat-Verbindung Schwierigkeiten. Eine tensieudiometrische Bestimmung zeigte, daß man das Wasser nur unter gleichzeitiger Zersetzung der Substanz bei etwa 300° abspalten kann. Man kann also letztlich nicht entscheiden, wieviel Wasser nun aus der Weinsäure und wieviel aus dem Konstitutionswasser stammt. Es wurde daher versucht, diese Frage auf andere Weise zu klären.

Eine bestimmte Menge (z. B. 34,0 mg) des Barium-Germanium-Tartrats wurde in der Hochvakuumapparatur mit einem Überschuß konzentrierter, ätherischer Lithiumalanat-Lösung (35 mg $LiAlH_4$/ml) versetzt, der sich entwickelnde Wasserstoff dann wie üblich tensimetrisch bestimmt. Während verdünnte Lithiumalanat-Lösungen mit wenig Wasser vornehmlich nach der Gleichung:

$$LiAlH_4 + 4\,H_2O = LiOH + Al(OH)_3 + 4\,H_2 \qquad (1)$$

reagieren, liegt der Umsetzung konzentrierter, d. h. etwa 3,5%iger Lösungen (wie sie hier zur Anwendung kamen) mit wenig Wasser hauptsächlich folgende Gleichung zugrunde:

$$2\,LiAlH_4 + 4\,H_2O = Li_2O + Al_2O_3 + 8\,H_2. \qquad (2)$$

Da die Weinsäure unter diesen Bedingungen von Lithium-Aluminiumhydrid nicht angegriffen wird, kann der sich entwickelnde Wasserstoff nur aus dem Konstitutionswasser stammen. Insgesamt wurden bei dieser, als Beispiel angeführten Bestimmung 0,355 mg Wasserstoff gefunden, was, da ja 1 Mol Wasserstoff 0,5 Mol Wasser entspricht (Gl. 2), 1,97 Mol Wasser ergibt.

Man kann also dem Barium-Germanium-Tartrat die empirisch ermittelte Formel

$$Ba_2GeC_8H_8O_{14} \cdot 2\,H_2O$$

zusprechen. Daraus errechnet sich ein Formelgewicht von 711,43. Der Umrechnungsfaktor für Germanium ergibt sich zu $F_{Ge} = 0{,}1020$ (empirisch gefunden $F_{Ge} = 0{,}102$). Über die Struktur des Barium-Germanium-Tartrats können noch keine endgültigen Aussagen gemacht werden; die vorliegende Arbeit hatte zunächst nur zum Ziel festzustellen, ob sich diese Verbindung zur quantitativen Abscheidung und Bestimmung des Germaniums eignet.

### *2. Die optimalen Fällungsbedingungen.*

Als Fällungsreagens für Germanium diente die von *Gautier* und *Pignard* zur Borbestimmung verwendete wässerige Lösung, die im Liter

240 g Ammoniumchlorid, 14 g Weinsäure und 13 g $BaCl_2 \cdot 2\ H_2O$ enthält. Sie wird im folgenden kurz „Lösung A" genannt.

Die Komplexbildung verläuft nur in Gegenwart von Ammoniak vollständig, und zwar hat sich ein Zusatz von 6 bis 7 ml 15-n Ammoniaklösung auf 10 ml der „Lösung A" als notwendig und ausreichend erwiesen.

Setzt man einen Überschuß eines derartigen Gemisches von „Lösung A" und Ammoniak zu einer Alkaligermanat-Lösung, so fällt bereits der größte Teil des vorhandenen Germaniums als Barium-Germanium-Tartrat aus. Dessen Löslichkeit ist aber noch zu groß, um vernachlässigt werden zu können. Sie beträgt in 100 ml Reagenslösung etwa 30 mg, so daß man stets zu tiefe Werte erhält und das Filtrat nie frei von Germanium ist.

Man kann aber die Löslichkeit des Barium-Germanium-Tartrats durch Acetonzusatz so weit verringern, daß keine Verluste an Germanium mehr auftreten. Es wurde zunächst versuchsweise eine Aceton-Menge entsprechend $^1/_{10}$ des Gesamtvolumens (das ist also Germanatlösung — „Lösung A" + Ammoniak) angewendet. Die Abscheidung des Germaniums erwies sich dann zwar als quantitativ, jedoch wurden stets zu hohe Werte erhalten. Für diese Unstimmigkeiten sind Okklusionserscheinungen verantwortlich zu machen, und zwar wird offenbar Bariumtartrat mitgerissen, dessen Löslichkeit in acetonhaltigem Medium ebenfalls stark zurückgedrängt wird. Es galt daher durch Reihenuntersuchungen die Acetonkonzentration aufzufinden, bei der die Ausfällung des Germaniums noch quantitativ war, ohne daß schon Okklusionen zu befürchten waren. Hierbei entsprach nur ein enger Bereich der Acetonkonzentration den gestellten Forderungen; weiterhin hat es sich auch als besonders vorteilhaft erwiesen, das Aceton erst nach dem Ausfällen der Hauptmenge des Germaniums zuzusetzen. Durch diese Arbeitsweise werden Störungen weitgehend ausgeschaltet, so daß die Formelreinheit des Niederschlages gewährleistet ist.

Diese bemerkenswerten Unterschiede in den Fällungsbedingungen des Barium-Germanium-Tartrats und denen des Bariumborotartrats (die Acetonkonzentration ist zur Abscheidung des letzteren weitaus nicht von so großer Bedeutung), werden von uns als Folge der im Vergleich zum Bariumborotartrat sehr viel größeren Komplexbildungsgeschwindigkeit des Barium-Germanium-Tartrats gedeutet.

Auf Grund dieser Untersuchungen läßt sich folgende *Arbeitsvorschrift* zur semimikrogravimetrischen Bestimmung des Germaniums angeben:

Zu 1 ml der zu untersuchenden, schwach alkalischen Alkaligermanat-Lösung, die bis zu 5 mg Germanium enthalten kann, setzt man in der Kälte Reagenslösung zu, die man sich unmittelbar vor der Fällung wie folgt bereitet: 5 ml der „Lösung A" + 3 bis 3,5 ml 15-n Ammoniak-

Lösung. Es empfiehlt sich, das Reagens unter Rühren zuzutropfen. Das Barium-Germanium-Tartrat fällt sofort als weißer, leicht flockiger Niederschlag aus. Nach etwa 10 Minuten gibt man zu dieser Suspension noch genau 0,5 bis 0,6 ml Aceton zu, worauf man nach abermals 10 Minuten durch einen Porzellanfiltertiegel G 2 abnutscht. Das Barium-Germanium-Tartrat ist stets leicht filtrierbar und haftet nicht an den Gefäßwänden. Man wasche mit einer Flüssigkeit, die im Liter 100 ml Aceton und 100 ml 15-n Ammoniak-Lösung enthält, bis im Filtrat kein Barium mehr als Sulfat nachweisbar ist. Zur Beschleunigung der bei 110° vorzunehmenden Trocknung wird mit Aceton nachgespült. Gewichtskonstanz wird bei 50 mg Niederschlagsgewicht nach etwa einer Stunde erreicht. $F_{Ge} = 0{,}1020$.

Bei Germaniummengen von 5 bis 10 mg/ml ist die Reagensmenge zu verdoppeln, d. h. also, es sind 10 ml der „Lösung A", 6 bis 7 ml 15-n Ammoniak-Lösung und nach der Fällung 1 bis 1,2 ml Aceton zuzusetzen.

Diese Vorschrift ist durch viele Beleganalysen gesichert, wovon einige hier angeführt seien (als Vergleichslösungen dienten durch Auflösen von reinstem Germaniumdioxyd in Natronlauge erhaltene Natriumgermanat-Lösungen):

Tabelle 1.

| Lösung A zugesetzt ml | ml 15-n $NH_3$ | Aceton ml | Angewendet mg Ge | Gefunden mg Ge | Differenz | |
|---|---|---|---|---|---|---|
| | | | | | mg | % |
| 3 | 2,0 | 0,3 | 0,117 | 0,12 | + 0,003 | + 2,0 |
| 5 | 3,5 | 0,5 | 1,27 | 1,27 | 0,00 | 0,0 |
| 5 | 3,5 | 0,5 | 1,27 | 1,23 | — 0,04 | — 3,1 |
| 5 | 3,5 | 0,6 | 2,54 | 2,59 | + 0,04 | + 1,9 |
| 5 | 3,5 | 0,5 | 4,68 | 4,53 | — 0,13 | — 2,7 |
| 5 | 3,5 | 0,5 | 4,68 | 4,73 | + 0,05 | + 1,2 |
| 7,5 | 5,0 | 0,75 | 6,35 | 6,35 | 0,00 | 0,0 |
| 7,5 | 5,0 | 0,75 | 6,35 | 6,33 | — 0,02 | — 0,3 |
| 7,5 | 5,0 | 0,75 | 6,35 | 6,39 | + 0,04 | + 0,6 |
| 15,0 | 10,0 | 1,50 | 12,70 | 12,76 | + 0,06 | + 0,5 |
| 20 | 14,0 | 2,0 | 19,10 | 19,11 | 0,0 | 0 |
| 50 | 35,0 | 5,0 | 52,41 | 52,2 | — 0,2 | — 0,4 |
| 50 | 35,0 | 5,0 | 63,5 | 63,8 | + 0,3 | + 0,5 |

Aus den Ergebnissen ist ersichtlich, daß man die Methode auch zur Bestimmung größerer Germanium-Mengen heranziehen kann.

Die durch Verdünnungsreihen ermittelte Erfassungsgrenze der Ausfällung von Germanium als Barium-Germanium-Tartrat liegt bei 0,1 $\mu$g/ml. Die Genauigkeit der Bestimmung liegt bei Germanium-Mengen von 10 bis 50 mg um 0,5%.

Neben der gravimetrischen Bestimmungsform besteht auch die Möglichkeit, das Germanium indirekt maßanalytisch zu bestimmen:

Man löst den Niederschlag in verd. Salzsäure, fällt das Barium als Chromat aus, filtriert, und bestimmt das Chromat dann wie üblich jodometrisch, wie es *Gautier* und *Pignard* schon beim Bariumborotartrat durchführten. Da diese Methode hier nichts prinzipiell Neues bringt, sei von einer näheren Beschreibung abgesehen.

### *3. Anwendungsbereich.*

Die Bestimmung des Germaniums als Barium-Germanium-Tartrat ist dann nicht möglich, wenn die Lösung Ionen enthält, die mit Barium schwerlösliche Niederschläge bilden, also z. B. $SO_4''$, $F'$, $CrO_4''$, $VO_4'''$, $WO_4''$, $PO_4'''$, $SiO_3''$, $TeO_3''$, $SeO_3''$ usw. Außerdem wird die Methode dann unbrauchbar, wenn in der Lösung Ionen vorhanden sind, die selbst schwerlösliche Bariumtartrat-Komplexe bilden. Zu diesen gehört natürlich die Borsäure, aber offenbar reagieren auch die Elemente der vierten Nebengruppe unter Bildung vielleicht ähnlich gebauter Verbindungen, zumindest aber Titan und Zirkon (Hf und Th wurden daraufhin noch nicht untersucht). Eine Ausarbeitung dieses Experimentalbefundes steht noch aus.

$Al^{+++}$, $Ga^{+++}$, $Fe^{+++}$, $Cr^{+++}$, $Sn^{--}$, maskiert als Weinsäurekomplexe, verhindern, sofern sie in großem Überschuß vorhanden sind, die Fällung von Barium-Germanium-Tartrat. Sofern aber die genannten Elemente in geringer Absolutmenge vorhanden sind und das Verhältnis Me : Ge nicht viel größer als 1 : 1 ist, gelingt auch dann noch die Abtrennung des Germaniums in zufriedenstellender Weise.

$Zn^{++}$, $Mg^{++}$, $Cu^{++}$ stören die Bestimmung nicht. $Pb^{++}$ stört erst in größeren Mengen. $Cd^{++}$ reagiert mit dem Ammoniumchlorid des Fällungsmittels unter Bildung schwerlöslicher Chlorokomplexe und muß daher vor der Germaniumbestimmung abgetrennt werden. Das Bariumborotartrat verhält sich in dieser Beziehung, wie wir der Erwartung gemäß feststellten, dem Barium-Germanium-Tartrat ganz ähnlich.

Es ist von Bedeutung, daß die Germaniumbestimmung nach dieser Methode auch noch in Gegenwart großer Mengen von Arsenit durchführbar ist, wie einige Beleganalysen zeigen:

Tabelle 2.

| Angewendet mg Ge | Zusatz von Ammoniumarsenit; berechnet in mg $As_2O_3$ | Gefunden mg Ge |
|---|---|---|
| 3,51 | 50 | 3,49 |
| 3,51 | 500 | 3,42 |
| 1,27 | 1000 | 1,30 |

Arsenat stört ebenfalls nicht, jedoch liegen hierüber vorerst nur qualitative Untersuchungsergebnisse vor. Bei extremem Arsenüberschuß

empfiehlt es sich, noch etwas Ammoniumchlorid zuzusetzen, da das Ausfallen von Bariumarsenit bzw. -arsenat bekanntlich in Gegenwart von viel Ammoniumsalz verhindert wird.

An dieser Stelle sei dem Direktor des Institutes für Anorganische Chemie, Herrn Prof. Dr. *E. Wiberg*, und dem Abteilungsvorstand, Herrn Prof. Dr. *M. Schmeisser*, für das mir erwiesene Wohlwollen, sowie Herrn Dipl. Chem. *H. Goeltzer* für die bereitwillige Förderung der Arbeit mein verbindlichster Dank ausgesprochen.

## Zusammenfassung.

Angeregt durch die Arbeit von *J. A. Gautier* und *P. Pignard* über die Borbestimmung als Bariumborotartrat wird nachgewiesen, daß das Germanat-Ion unter fast analogen Bedingungen ein dem Bariumborotartrat offenbar ähnliches Barium-Germanium-Tartrat der empirisch ermittelten Formel $Ba_2GeC_8H_8O_{14} \cdot 2\,H_2O$ bildet. Diese neue Komplexverbindung des Germaniums wird auf ihre analytische Verwendbarkeit hin geprüft und auf Grund der Untersuchungsergebnisse eine neue Methode zur Bestimmung des Germaniums angegeben. Ein verhältnismäßig günstiger Umrechnungsfaktor ($F_{Ge} = 0{,}1020$), die Einfachheit des Verfahrens und dessen Schnelligkeit gewähren eine elegante Bestimmungsmöglichkeit des Germaniums; es eröffnen sich für bestimmte Fälle auch neue Abtrennungsmöglichkeiten, wobei von besonderer Bedeutung ist, daß die Bestimmung auch neben viel Arsenit (und wahrscheinlich auch Arsenat) möglich ist.

## Summary.

Stimulated by the study by *J. A. Gautier* and *P. Pignard* of the determination of boron as barium borotartrate, it has been shown that under practically analogous conditions the germanate ion forms a barium germanium tartrate of the composition $Ba_2GeC_8H_8O_{14} \cdot 2\,H_2O$, which in all probability is similar to the barium borotartrate. This new complex compound of germanium was tested with respect to its analytical usefulness and a new method of determining germanium was worked out on the basis of the findings. Because of the relatively favorable conversion factor ($F_{Ge} = 0.1020$), and the simplicity of the procedure and its rapidity, there is a good possibility of an elegant method of determining germanium. Furthermore, in certain cases, there are new possibilities of separations, in which special importance attaches to the fact that the determination is possible even in the presence of much arsenite (and probably also arsenate).

## Résumé.

Sous l'instigation du travail de *J. A. Gautier* et *P. Pignard* sur le dosage du bore en borotartrate de baryum, on a recherché si l'ion germanique, dans des conditions presque analogues pouvait donner un germanotartrate de baryum de formule vraisemblablement identique $Ba_2GeC_8H_8O_{14} \cdot 2\,H_2O$. Ce complexe nouveau a été essayé pour son emploi analytique et l'on donne une nouvelle méthode de dosage du germanium sur la base des résultats de recherche. Un facteur d'analyse particulièrement favorable ($F_{Ge} = 0{,}1020$),

la simplicité du procédé et sa rapidité s'accordent pour une élégante possibilité de dosage du germanium; sont possibles également pour des cas spéciaux de nouvelles séparations d'importance particulière, le dosage à côté de beaucoup d'arsénite (et probablement aussi d'arséniate).

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# The Microdetermination of Nitrogen in Organic Compounds by the Rapid Combustion Process.

By

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With 3 Figures.

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## Introduction.

The *Pregl-Dumas* method of determining nitrogen has the disadvantage of being time-consuming and is also subject to errors. High results are sometimes obtained because the movable filling of copper oxide with which the sample is mixed contains some adsorbed nitrogen. Low results are obtained with certain types of organic compounds, polyacrylonitrile being a typical example, yielding nitrogenous chars which cannot be burned away completely owing to a lack of oxygen.

Several of the modifications to the method have been concerned with procedures which generally overcome the above two disadvantages. Thus, the use of oxygen for the combustion has been advocated by *Unterzaucher*[1] and others[2]. This innovation permits the sample to be introduced into the combustion tube in a platinum boat, and thus the source of high blank error is considerably reduced by the absence of the movable filling of copper oxide. Simultaneously, nitrogenous chars are completely burned away in the presence of the oxygen.

By modifying the procedure other workers have cut down the working time of the analysis. *Colson*[3] for example, has found that a much faster carbon dioxide stream could be employed, by extending the normal length of metallic copper to 20 cm, without affecting the completeness of reduction of nitrogen oxides formed during the combustion. Whereas *Colson*'s method reduces the analysis time to about 40 minutes, *Schöniger*[4], by employing a pre-combustion technique, has cut the working time to even lower limits. In the latter's method the sample is mixed with copper oxide as usual, but in a short combustion tube attached to a longer tube which contains the normal filling of copper oxide and

metallic copper. This procedure permits the main tube to be kept in a prepared state during a series of analyses, and allows as many as four determinations to be made in an hour. The rapidity of the method is achieved by exchanging the pre-combustion tube with another sample-filled tube as soon as all the nitrogen has been swept into the nitrometer. This, and *Colson*'s method, have the disadvantage that they cannot be applied to samples which yield nitrogenous chars.

*Kirsten*[5] has employed the reaction:

$$C + CO_2 = 2\,CO$$

for burning compounds which combust only with difficulty, but he introduces a different tube filling from that used in the *Pregl-Dumas* method, and employs a flow rate of 10 ml per minute. The sample, in a boat, is burned at 1050° C, and the decomposition products are led over nickel oxide and metallic nickel held at 1000° C. Residual carbon monoxide is removed from the gas-stream by means of "Hopcalite" placed in the beak-end of the combustion tube.

Whereas the method of *Kirsten* is one employing new principles, the recent modifications of the *Pregl-Dumas* method indicate two important trends of development, namely: (1) the introduction of oxygen, which appreciably widens the range of the method, and (2) the adoption of techniques which speed up the course of the determination. So far however, no method has been developed having the best possible conditions for combustion, and combining the two advantages of rapidity and wider application afforded by the use of oxygen. A method based on the rapid combustion process which would have these advantages was envisaged by the present author following experience gained in extending the "empty tube" principle of combustion[6]. It was considered that, since it had been established that organic compounds are completely oxidised when burnt in a fast stream of oxygen without an additional catalyst, the principle could be adapted under suitable conditions to determine nitrogen. The present paper records the difficulties encountered and the experience gained in the development of such a method.

## Principle of the Method.

The principle of the method is that the sample, in a platinum boat, is vaporised and burned in a fast stream of carbon dioxide-oxygen mixture, in a combustion tube of the design employed by *Belcher* and *Ingram* in their rapid method for carbon and hydrogen. The combustion products are led over heated copper, thus removing excess of oxygen and reducing the oxides of nitrogen in the gas-stream. The nitrogen remaining is swept out with the transport gas into a nitrometer, collected over potash solution and measured. A single determination may be completed in

about 20 minutes, which includes the necessary cooling period prior to measuring the volume.

## Experimental.

Four important variables had to be considered in adapting the rapid combustion principle to the determination of nitrogen, notably (1) the source of oxygen, (2) the oxygen–carbon dioxide ratio, (3) the flow rate and (4) the length of metallic copper.

### *The Source of Oxygen.*

Medicinal oxygen was first employed, and was fed into the gas-stream from a cylinder of the gas metered down in the usual manner. The pressure of the gas mixture delivered to the combustion tube was controlled by means of a T-type regulator, and was measured by means of a flow meter. Rates of flow in the range of 10–50 ml per minute were tried. Two kinds of blank determination were run over this range of flow rates: The *oxygen* blank, to determine the amount of inert gas contained in the oxygen; the *combustion* blank, to determine the extent of combustion under the various flow rates. Comparable average times were employed so that a similar volume of gas mixture was used in each of the determinations. A series of blanks was also made passing carbon dioxide alone through the combustion tube, both at its working temperature, and in the cold, to determine to what extent dissociation of carbon dioxide occurred at the higher temperature. The results of these experiments are given in Table 1. They indicate that the cylinder oxygen contained

Table 1.

| Flow ml/min. | Duration time min. | Oxygen blank ml N. T. P. | Combustion blank | | $CO_2$ blanks | |
|---|---|---|---|---|---|---|
| | | | mg benzoic acid | ml N. T. P. | Hot* ml N. T. P. | Cold ml N. T. P. |
| 10 | 20 | 0.032 | 4.65 | 0.042 | 0.004 | 0.003 |
| | | 0.04 | | | | |
| 20 | 10 | 0.03 | 3.655 | 0.037 | 0.003 | 0.003 |
| | | 0.025 | | | | |
| 30 | 6 | 0.036 | 3.873 | 0.049 | 0.004 | 0.004 |
| | | 0.028 | | | | |
| 40 | 5 | 0.037 | 4.005 | 0.052 | 0.005 | 0.002 |
| | | 0.032 | | | | |
| 50 | 5 | 0.05 | | | 0.005 | 0.003 |
| | | 0.042 | | | | |
| 20 | 15** | 0.04 | 4.255 | 0.051 | 0.005 | 0.004 |

* Temperature of combustion chamber was 800° C and the copper layer 650° C.

** In this experiment the combustion was carried out more slowly.

appreciable amounts of inert gases, and that the method of mixing the two gases was unsatisfactory because the *oxygen* blank was inconsistent over the range of flows. The slightly higher *combustion* blanks showed that at rates between 20 and 40 ml per minute combustion was not complete. The results of the *carbon dioxide* blanks showed that no dissociation of the gas at the higher temperature of the combustion tube was evident over the range of flows.

Because of the inconsistency of the *oxygen* blank, controlled tests were carried out with the gas mixture containing a known amount of oxygen. For these experiments the mixture was delivered from a 400-ml reservoir using a flow rate of 20 ml per minute, and passing 300 ml of the gas mixture. The results of the *oxygen* and *combustion* blanks are given in Table 2. These indicate the true value of the blank and the extent of combustion.

Table 2.

| Ratio $CO_2$:O | Oxygen blank ml N. T. P. | Combustion blank | |
|---|---|---|---|
| | | mg benzoic acid | ml N. T. P. |
| 10:1 | 0.015 | 3.76 | 0.068 |
| | 0.017 | 5.86 | 0.085 |
| 5:1 | 0.026 | 3.684 | 0.035 |
| | 0.024 | 2.548 | 0.048 |
| 5:2 | 0.034 | 4.685 | 0.048 |
| | 0.043 | 3.965 | 0.056 |
| 5:3 | 0.068 | 4.233 | 0.071 |
| | 0.065 | 3.216 | 0.069 |
| 1:1 | 0.096 | 3.652 | 0.103 |
| | 0.102 | 2.373 | 0.093 |

In these experiments a flow rate of 20 ml/min. was used, passing 300 ml of gas mixture.

Although it was evident that combustion would apparently be complete employing a carbon dioxide–oxygen mixture in the ratio of 5:3. it was concluded that the *oxygen* blank was far too high for accurate work. In addition it was considered that the control needed for delivering the gas mixture would increase the tediousness of the method rather than simplify it.

When in 1950 *Unterzaucher* recommended the catalytic reduction of hydrogen peroxide as a source of oxygen, further tests were made. These however, proved that while the *combustion* blank was negligible with a fresh solution of the reagent, the rate of evolution could not be controlled satisfactorily, and it diminished very quickly. After a few *combustion* blanks had been made, the volume of gas collected reached a value of

0.2 ml, which was assumed to be carbon monoxide, since *carbon dioxide* blanks were below 0.01 ml.

Electrolytic oxygen, being virtually free from inert gases, was next tried, and proved superior to other sources of the gas. For its generation, a cell was constructed which could be inserted permanently in the combustion train. This innovation has many advantages. For example, the rate of evolution of the oxygen can be accurately controlled and any desired ratio of oxygen–carbon dioxide may be obtained by a simple adjustment of the cell current. The apparatus once set up needs no further attention to give a continuous supply of blank-free oxygen. A continuous supply of hydrogen is also available to enable the copper filling in the combustion tube to be regenerated, daily if necessary, with the minimum of trouble.

*Construction of the Generator.*

The apparatus is shown in detail in Fig. 1. It is constructed entirely of borosilicate glass, rubber connections being avoided to minimise the

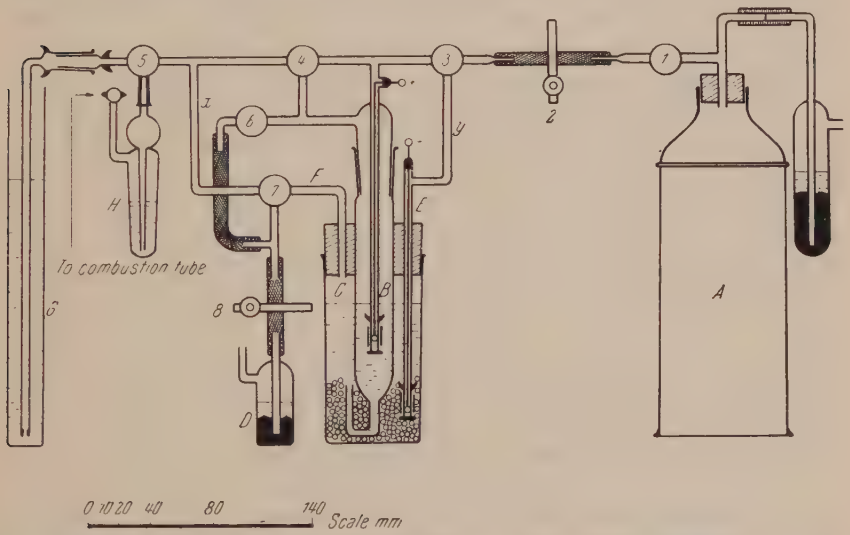


Fig. 1. Electrolytic Generator and Gas Control Systems. *A* Carbon dioxide generator. *B* Oxygen evolution chamber. *C* Hydrogen evolution chamber. *D* Gas escape valve. *E* Delivery tube to hydrogen chamber. *F* Hydrogen outlet. *G* Pressure regulator. *H* Bubble-counter or flowmeter. 1 Carbon dioxide control stopcock. 2 Precision screw-clip for fine control of carbon dioxide. 3 Three-way stopcock. 4 Three-way stopcock. 5 Three-way stopcock. 6 One-way stopcock. 7 Three-way stopcock. 8 Precision screw-clip.

possibility of leaks. The generator consists of the oxygen evolution chamber *B*, the hydrogen evolution chamber *C*, a gas escape valve *D*, a pressure regulator *G*, and a bubble-counter *H* for measuring the gas

flow. The outer electrolytic cell is a tall-form 250-ml beaker closed by a tight-fitting rubber bung, which is sufficient for making this part of the cell gas-tight. Through the bung is inserted the long tubular oxygen chamber, an inlet tube *E*, an outlet *F* for the hydrogen gas, and a filling tube (not shown) closed by a ground-glass stopper. Thick-walled, 2.5–3 mm bore glass tubing is used to connect the parts of the system together. In constructing the generator, the ground-glass joint situated at the top of the oxygen cell is made gas-tight with sealing cement before fusing the two main parts of the cell together. This is conveniently accomplished at the points *x* and *y*. Alternatively, sealing may be avoided by employing small ground-glass joints at these two points.

The cell is filled to within about 25 mm of the bung with a 10% air-free solution of sulphuric acid introduced through the filling tube. The glass beads in the bottom of the beaker add weight to the vessel and, with the U-shaped connecting tube attached to the base of the oxygen cell, form an efficient gas barrier between the two evolution chambers.

The two electrodes are made from strips of thin platinum gauze 15 mm wide and about 60 mm long. These are wound over the sealed lower ends of the gas delivery tubes so that the gauze covers two 2-mm holes situated opposite each other in the walls of the tubes about 7 mm from the closed ends. By this means the transport gas is intimately mixed with the gases evolved at the electrodes. The gauzes rest on the flanged ends of the tubes and are held securely by hooks sealed to the tubes. Their connecting leads of platinum wire pass through one of the gas delivery holes and proceed up the tubes to tungsten terminals sealed in the outer walls of the tubes.

A cell current of 10–15 volts D. C., 0.5–0.7 amp., was found to produce sufficient oxygen in the generator described, to bring about complete combustion. The current was supplied from a 110 volt D. C. source through a variable resistance in conjunction with a voltmeter and ammeter to measure the current.

### *Operation of the Generator.*

The generator functions as follows: Carbon dioxide from the "Drikold" source *A*, of Fig. 1, is metered down with the precision screw-clip 2 and passes through the stopcock 3 which permits the gas to proceed through the outer chamber giving a mixture of the transport gas and hydrogen; or, alternatively, through the central chamber giving a mixture of oxygen and the transport gas. The mixture of gases then passes respectively through stopcock 7 or 4 through the bubble-counter to the combustion tube. When carbon dioxide alone is required stopcocks 3 and 4 are adjusted accordingly.

When current is applied to the electrodes, as during a combustion, the hydrogen evolved escapes through the valve *D* into the atmosphere through stopcock 7. The valve contains a 5–10 mm layer of mercury topped by a little paraffin which prevents mercury vapour being carried into the atmosphere. The hydrogen is led away from the proximity of the apparatus by rubber tubing to a fume hood or other suitable place.

Pressure equilibrium is established between the two chambers by adjusting the precision screw-clip provided on the rubber tube between the hydrogen outlet and the gas valve. Thereafter, any pressure increase caused by a rise of gas volume in the outer chamber is balanced out by means of the pressure regulator. The pressure regulator also functions when oxygen is being evolved and the selected flow rate has been established by means of the carbon dioxide precision screw-clip control. Increased pressure due to oxygen evolution is balanced out by the regulator, and the flow rate is maintained throughout the course of the combustion.

For the regeneration of the copper, the transport gas is diverted to the outer chamber of the generator, stopcock 4 is turned to cut off the oxygen system from the main gas-stream, and the hydrogen mixture passes to the combustion tube via stopcock 7. The oxygen evolved is then allowed to escape into the atmosphere by opening stopcock 6, regulating the gas valve screw-clip to establish the proper pressure equilibrium. It is advantageous to increase the cell current to about 0.9 amp. so that more hydrogen is made available for the reduction. At the same time the regulator *G* may be cut off by means of stopcock 5, for its functioning in this instance is immaterial.

The gas stream is dried by means of anhydrone contained in a *Pregl* U-tube inserted between the bubble-counter and side-arm of the combustion tube.

### *The Flow Rate.*

Many determinations were made, using a wide range of flow rates of the carbon dioxide–oxygen mixture, to establish the most satisfactory value which would produce complete combustion, and at the same time permit complete removal of the excess oxygen and complete reduction of the nitrogen oxides by the hot copper. The most satisfactory results were obtained with a flow rate in the range of 15–20 ml per minute, permitting a combined combustion and sweeping period of under 15 minutes. The results are summarized in Table 3. It is notable that though almost theoretical figures were obtained at high flow rates where the nitrogen in the sample is linked to carbon or hydrogen, some low results were obtained with nitro-compounds. This discrepancy may be explained by the fact that nitro-compounds yield almost all their nitrogen as oxides[7], which are not completely reduced at the higher flow rates because of

Table 3.

| Sample | Weight mg | Flow ml/min. | Found N%* | Required N% | Duration time min. |
|---|---|---|---|---|---|
| Dinitrobenzene | 3.573 | 13 | 16.43 | 16.66 | 12 |
| | 3.694 | 15 | 16.64 | | 13 |
| | 3.094 | 15 | 16.67 | | 12 |
| | 3.694 | 15 | 16.79 | | 17 |
| | 3.287 | 16 | 16.8 | | 11 |
| | 2.733 | 16 | 16.43 | | 9 |
| | 3.191 | 25 | 16.3 | | 8 |
| | 3.623 | 25 | 15.26 | | 7 |
| | 3.715 | 30 | 15.88 | | 8 |
| | 3.836 | 36 | 15.32 | | 6 |
| | 3.475 | 36 | 15.0 | | 5 |
| | 3.447 | 36 | 15.56 | | 6 |
| | 2.518 | 40 | 14.88 | | 8 |
| | 3.499 | 44 | 15.71 | | 6 |
| | 3.637 | 50 | 14.30 | | 5 |
| Dinitrophenol | 3.786 | 15 | 15.4 | 15.2 | 15 |
| | 3.84 | 15 | 15.0 | | 16 |
| Dimethylglyoxime | 3.225 | 4 | 21.9 | 24.1 | 45 |
| | 2.685 | 7 | 22.02 | | 28 |
| | 1.647 | 10 | 21.72 | | 15 |
| | 2.811 | 13 | 24.0 | | 13 |
| | 2.78 | 15 | 23.82 | | 25 |
| | 2.773 | 16 | 23.84 | | 10 |
| | 3.347 | 16 | 24.05 | | 10 |
| | 3.373 | 36 | 23.97 | | 6 |
| | 3.05 | 36 | 24.02 | | 8 |
| Acetyl sulphanilamide | 3.954 | 15 | 13.02 | 13.1 | 11 |
| | 3.499 | 15 | 12.9 | | 24 |
| | 3.594 | 16 | 13.3 | | 7 |
| | 3.601 | 20 | 13.16 | | 11 |
| | 2.052 | 20 | 13.2 | | 25 |
| Acetanilide | 2.865 | 16 | 10.42 | 10.4 | 7 |
| | 3.615 | 16 | 10.56 | | 12 |
| Phenacetin | 3.928 | 15 | 7.89 | 7.82 | 14 |
| | 3.249 | 20 | 7.87 | | 10 |
| | 3.767 | 25 | 7.75 | | 10 |
| p-Diacetoxyazobenzene | 4.055 | 16 | 9.32 | 9.4 | 12 |
| | 3.459 | 16 | 9.3 | | 10 |
| Azobenzene | 3.643 | 15 | 15.4 | 15.4 | 11 |
| | 2.802 | 20 | 15.36 | | 6 |
| Polyacrylonitrile | 2.625 | 10 | 25.53 | 26.4** | 15 |
| | 2.636 | 16 | 25.64 | | 13 |
| | 1.94 | 16 | 25.51 | | 15 |
| | 3.696 | 20 | 25.58 | | 10 |

* Corrected values.

** Found by *Kjeldahl* 25.55% N. By *Pregl-Dumas* 18.95% N.
25.69

the greater concentration of gases and high rate of flow. Nitroso–compounds yield a much lower proportion of nitrogen oxides and therefore the concentration is lower and complete reduction of the oxides of nitrogen is possible.

Negligible *oxygen* and *combustion* blanks indicated complete freedom from inert gases and complete combustion at the various flow rates. *Carbon dioxide* blank determinations showed that dissociation of the transport gas was negligible. Some blank values obtained on burning samples of benzoic acid and naphthalene are given in Table 4 together with other blank values.

### *Measurement of the Flow Rate.*

Although the bubble-counter adequately measures the flow rate, it was later found more convenient to utilise a flow-meter for this purpose.

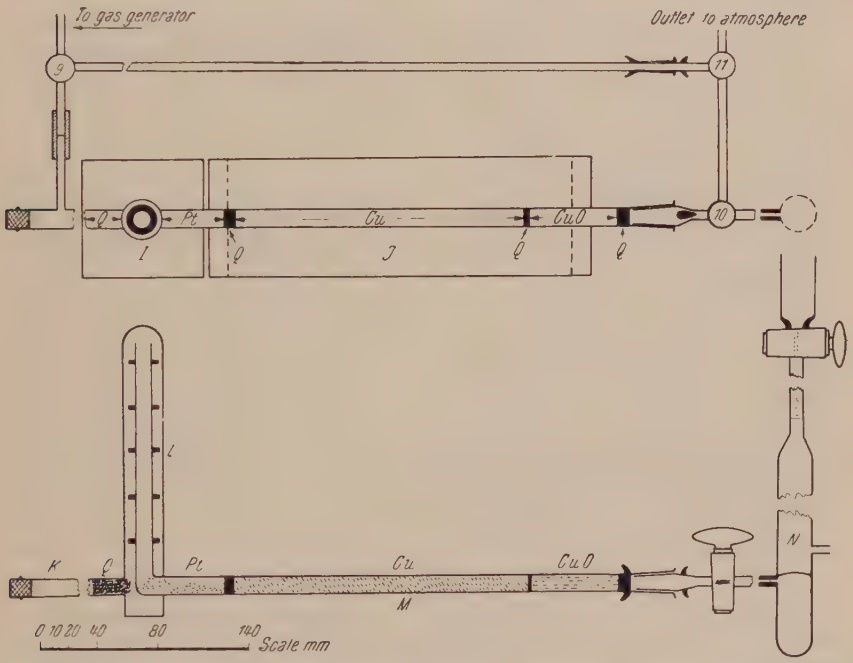


Fig. 2. Combustion Tube and Reverse Flushing System. *I* Combustion chamber furnace – 800° C. *J* Copper layer furnace – 650° C. *K* Sample vaporising section of combustion tube. *L* Combustion chamber. *M* Nitrogen oxides reduction and oxygen removal section. *N* Nitrometer. *Q* Quartz wool. 9 Three-way stopcock. 10 Three-way stopcock. 11 Three-way stopcock.

Because the usual pattern is difficult to make air-free, one was designed from which the air could easily be replaced by carbon dioxide.

The construction of the flow-meter is shown in Fig. 3. Air in the manometer tube *A* is replaced by carbon dioxide as follows: Stopcock 9

(Fig. 2) is turned to cut off the gas supply to the combustion tube, then the capillary *B* (Fig. 3) is by-passed by means of the three-way stopcock *C*, and the ground-glass stopper *D* situated at the bottom of the capillary chamber is turned to connect with an outlet *E* provided in the walls of the stopper. Carbon dioxide then passes down the manometer tube through the liquid in the bulb, and escapes into the atmosphere.

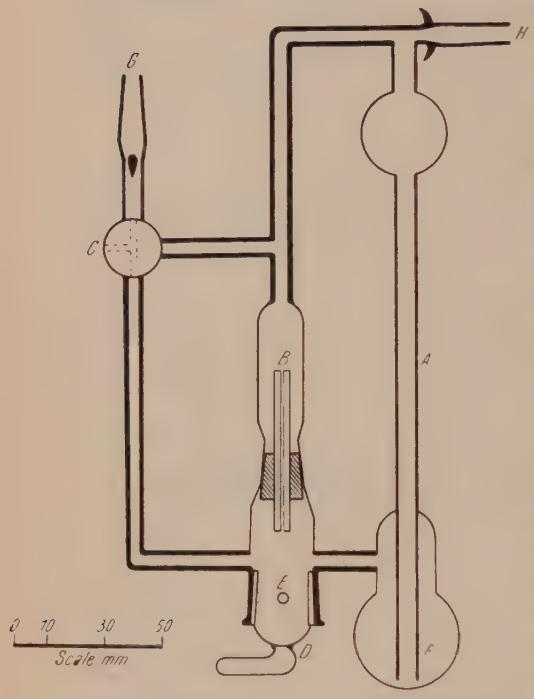


Fig. 3. Air-Free Flowmeter. *A* Manometer tube. *B* Capillary. *C* Three-way stopcock. *D* Ground-glass stopper tap. *E* Outlet hole. *F* Manometer fluid reservoir. *G* Connection to gas generator. *H* Connection to combustion tube.

The manometer is calibrated in the usual manner with a Mariotte bottle, adding the required volume of liquid to the pressure regulator to give a flow rate of 15 ml per minute. Paraffin is a convenient liquid to place in the pressure regulator tube; a silicone oil is a suitable manometer fluid.

### *The Copper Layer.*

Copper layers of 10, 15 and 20 cm respectively were tried, and it was found that though amino-compounds were always analysed successfully employing a 10 cm layer of copper, a 20 cm length was more efficient, particularly in the case of nitro-compounds, and required less frequent regeneration. Generally the copper required reducing after every 20 determinations.

### *Preparation of the Copper.*

Careful preparation of the copper is essential, otherwise a less active reagent of lower efficiency is obtained. It is best prepared as follows. Copper oxide of M. A. R. grade, in wire form, is broken into 3–4 mm lengths and screened to remove dust and the finer particles. It is then placed in a beaker containing a 10% solution of acetic acid and boiled for at least 15 minutes. After pouring off the acid solution, the copper oxide is washed free of acid with hot distilled water. The reagent is then removed to a dish and dried in the oven. Sufficient of the dry reagent is packed into a clean piece of combustion tubing and ignited in a stream of pure oxygen. When cool, the copper oxide is removed

from the tube and screened once more to separate any fine particles. Then it is repacked into another clean piece of combustion tubing for its reduction with hydrogen. This is carried out by heating the copper oxide at 250–300° C by means of an electric furnace, using a moderately slow stream of hydrogen diluted with carbon dioxide. The reduced material is allowed to cool in a slow stream of hydrogen. It is then removed from the tube and any pieces sticking together are separated before being packed into the combustion tube.

*The Combustion Tube.*

This, with the exception of the chamber outlet tube, has the same design and dimensions as the combustion tube described for the determination of carbon and hydrogen[6]. The outlet tube sealed to the chamber, and containing the metallic copper, is 300 mm long, has a bore of 9–10 mm, and terminates with a standard B 14 socket joint for connection to the reverse flow system and the nitrometer.

The tube is packed with copper as follows. A 60-mm long roll of fine-mesh platinum gauze is pushed to the elbow of the chamber outlet and is followed by a 10 mm wad of quartz wool which is tapped hard against the gauze. Next the prepared copper is introduced to form a layer 200 mm long which is held in place by a 5 mm wad of quartz. The copper is introduced carefully a few centimetres at a time, being tapped downwards after each addition, so that when the section is filled channelling of the filling does not occur. Finally, a 60 mm layer of washed and ignited copper oxide (wire form and in 4–5 mm lengths) is introduced, being held in position with a 7–10 mm wad of quartz wool. It is essential to have the layer of copper oxide in the tube to oxidise traces of carbon monoxide remaining in the gas stream.

The combustion chamber of the tube is maintained at 800° C by means of the split-type furnace designed for the chamber-type of combustion tube[6]. The copper section is held at 650° $\pm$ 10° C also by a split-type furnace. Its effective heating length must be 230 mm so that the entire length of copper and 30 mm of the copper oxide is heated.

The combustion tube is provided with a reverse flushing system through three-way stopcocks 9, 10 and 11 of Fig. 2, so that carbon dioxide may be passed in the reverse direction through the tube while the sample is being introduced and thus prevent ingress of air.

*Blank of the Method.*

The "method blank" is composed of the combined values of the *carbon dioxide, oxygen,* and *combustion* blanks. Experience has shown that this combined value is generally small, being in the order of 0.005–0.01 ml, and is constant over long periods. Blank values above this range may

arise from many sources, notably from occluded air in the carbon dioxide supply, leaks from faulty connections, and carbon monoxide formation. Both "Drikold" and "Cardice" brands of commercial solid carbon dioxide have been used by the present author for many years, and have not given trouble arising from occluded air. By using properly lubricated ground-glass joints, leaks may be avoided completely. As regards carbon monoxide formation, this is negligible, despite a large amount of metallic copper in the combustion tube. Carbon monoxide has been obtained only when the oxygen concentration in the mixture was too low, resulting in incomplete combustion of the sample. The short layer of copper oxide following the metallic copper is sufficiently long enough to remove traces of the gas remaining in the gas stream.

*Other Sources of Error.*

There has been no evidence of the copper layer failing to retain the excess of oxygen completely and thus introduce an appreciable error into the analysis. Tests have shown that a high concentration of oxygen in the combustion mixture has a negligible effect on the *oxygen* blank, and the copper layer is effective until almost all the metal has been oxidised.

The most serious source of error leading to faulty blank values arises from porosity of the quartz combustion tube. With a new tube blank values were in the range of 0.003–0.01 ml, but after some weeks of use this value gradually increased to 0.02 ml, and eventually reached the figure of 0.05 ml. An investigation of this source of error revealed that the section of the tube containing the copper was at fault, and that the empty chamber section was not subject to porosity (see Table IV). From this it may be concluded that quartz is not an ideal material for combustion tubes, at least for the nitrogen determination. This is contrary to general findings, for quartz combustion tubes have been used in micro-combustion methods for many decades without giving this trouble. It is only in recent years that the porosity phenomenon has arisen. One possible explanation is that present-day quartz tubing contains some impurity capable of catalysing the reduction of the quartz material, leading eventually to porosity of the tube walls. Contrary to this reasoning is the fact that no evidence has been obtained of similar porosity of tubes used in the apparatus for the determination of carbon and hydrogen. It must be assumed therefore that the presence of oxygen in the tube prevents reduction of the quartz material. Thus the combustion chamber of the nitrogen tube shows no apparent porosity even after weeks of use, whilst the copper containing part of the tube, which is always filled with an inert atmosphere, may show the defect after a few days.

Another possibility not to be overlooked is that the copper itself contains catalytic impurities which are not removed by the acid treatment,

Table 4.

| Compound | Flow ml/min. | Combustion blank ml N. T. P. | $CO_2$ blank hot ml N. T. P. | Duration time min. |
|---|---|---|---|---|
| | 10 | | 0.008 | 20 |
| | 15 | | 0.01 | 15 |
| | 20 | | 0.012 | 10 |
| | 36 | | 0.01 | 10 |
| Benzoic acid, 3–5 mg samples..... | 10 | 0.015 | | 20 |
| | 15 | 0.014 | | 15 |
| | 16 | 0.015 | | 12 |
| | 20 | 0.014 | | 10 |
| | 36 | 0.012 | | 10 |
| Naphthalene, 3–5 mg samples..... | 5 | 0.007 | | 25 |
| | 10 | 0.005 | | 20 |
| | 15 | 0.002 | | 10 |
| | 20 | 0.005 | | 10 |
| | 25 | 0.004 | | 10 |
| *Porosity tests* | | | | |
| | 15 | 0.050 | | 12 |
| | 15 | | 0.052 | 12 |
| Chamber furnace off ..... | 15 | | 0.050 | 12 |
| $CO_2$ blank-cold furnaces ..... | 15 | | 0.004 | 12 |
| Chamber furnace on ..... | 15 | | 0.007 | 12 |
| Copper removed– | | | | |
| Chamber furnace on ..... | 15 | | 0.005 | 12 |
| Both furnaces on..... | 15 | | 0.052 | 12 |
| Copper furnace on–tube empty ... | 15 | | 0.043 | 12 |

and thus may cause the defect. An investigation into this probable source of reduction is being carried out.

The life of the tube is considerably lengthened by carefully cleansing the quartz tubing prior to constructing the combustion tube. The treatment consists of first cleaning the surfaces of the tubing with hot soapy water, followed by copious washings with water, and then with distilled water. Next, after sealing up one end of the length of tubing, it is filled with 40% hydrofluoric acid solution and left to soak for at least one hour. Then the acid is poured out, and the tube is washed once more with distilled water. The tubing when dry is ready for constructing the combustion tube. Before doing so, the entire length of the tubing is heated to the softening point and blown to an even wall-thickness. This second treatment produces an extremely clear sample of quartz tubing, and it remains non-porous for a longer period than the untreated tubing.

Low results are attributable to incomplete reduction of nitrogen oxides by the copper, due to various causes. The copper oxide for the

preparation of the copper must not be reduced *in situ* by packing the combustion tube with the oxide. The filling will shrink during reduction and lead to channelling, and consequently some oxides of nitrogen will escape reduction. The copper oxide, and subsequent reduction of the copper filling in the combustion tube must be carried out at between 250–300° C otherwise the active nature of the reagent will be lowered. Whereas the copper layer will retain oxygen completely until all but a few centimetres of the reagent remains, short lengths of the copper will not cope with the rapid stream of gases and reduce completely the nitrogen oxides present. For this reason the layer must be reduced as soon as some 10 cm of it has been used up by the oxygen retained. The reduction should be carried out as described later.

## Method of Analysis.

After assembling the apparatus as shown in Fig. 1 and 2, the procedure consists of establishing the flow rate of 15 ml per minute; testing for leaks by a series of *carbon dioxide* blanks with the combustion tube at room temperature; and finally establishing the "method blank" by burning a few milligrams of benzoic acid or other similar type of compound. The blank is carried out in the same manner as a determination, introducing about 0.3 ml air into the nitrometer so that any increase in volume due to the blank may be determined accurately. The fast stream of bubbles ascending the nitrometer liquid does not interfere in any way with observation of the size of the bubbles.

### *Procedure for Introducing the Sample.*

The carbon dioxide flow is reduced by closing the precision screw-clip of the "Drikold" generator. Stopcocks 3, 4, 9 and 11 are turned so that the gas flow by-passes the electrolytic cell and the combustion tube, and proceeds into the atmosphere through the outlet of stopcock 11. The carbon dioxide is then turned on, and stopcock 5 to the pressure regulator is closed, so that a fairly fast stream of gas sweeps through the by-pass tube to stopcock 11. After one minute, stopcock 10 and 11 are turned so that the gas flow is reversed through the combustion tube. The stopper of the tube is then removed, and the boat containing the sample is introduced and pushed with a glass rod to within 60–70 mm of the furnace. The flow is increased to 20 ml per minute for 30 seconds, whereupon the stopper is replaced and firmly seated in the mouth of the combustion tube.

Stopcock 9 is turned to its original position, and stopcock 11 is connected with 10 so that the sweeping gas passes into the atmosphere once more to remove the last traces of air from the apparatus. After

3 minutes sweeping with a fast flow; the flow is decreased, stopcock 10 is connected with the nitrometer. If microbubbles are obtained the combustion is carried out as follows.

*The Combustion.*

Turn stopcocks 3 and 4 so that carbon dioxide bubbles through the oxygen cell, and open the pressure regulator stopcock. Connect *F* with the escape valve and adjust the transport gas flow to 15 ml per minute with the precision screw-clip of the gas control. Switch on the cell current, and adjust the cell pressure with the screw-clip of the gas valve. Wait one minute for the chamber of the combustion tube to be swept with the oxygen mixture, light the burner, and place it with the tube flame-spreader behind the sample container. Then proceed with the combustion using the normal rapid combustion technique. About 7 minutes should be taken to move the burner up to the furnace, then the tube between the boat and the furnace is heated strongly to burn any carbonaceous material deposited. When about 150 ml of gas has passed through from commencement of the combustion, the oxygen generator current is switched off, and stopcocks 3 and 4 are turned so that carbon dioxide only is passing through to sweep out the last traces of nitrogen into the nitrometer. When microbubbles are obtained once more, extinguish the burner, turn stopcock 10 to connect with 11 and the atmosphere, and raise the nitrometer reservoir to its upper position. Read the volume of nitrogen in the usual way after a standing period of 10 minutes. Meanwhile, weigh out the next sample, introduce it into the tube and commence sweeping out in readiness for the combustion.

*Volume Corrections.*

Two corrections of the volume measured are necessary to arrive at the true figure. The empirical correction of 1.2% of the volume of nitrogen due to adhesion of the potash solution to the nitrometer wall, and to the vapour pressure of the solution, is subtracted, and the corrected volume reduced to normal temperature and pressure. From this volume is then deducted the "method blank", also corrected to normal temperature and pressure.

*Regeneration of the Copper Layer.*

This operation may be carried out while the furnaces are heating up to their working temperatures at the start of a series of analyses. The control of the copper furnace is set so that its temperature does not exceed the maximum of 300° C. The water formed during the reduction is allowed to escape by removing the nitrometer at the ground-glass joint, to permit the water to be driven out quickly from the combustion tube.

When the copper layer has been reduced completely the filling is swept out for about 15 minutes with carbon dioxide. Then the temperature of the furnace is brought up to its working figure, after which the nitrometer is attached once more to the combustion tube.

## Summary.

A method is described for the microdetermination of nitrogen in organic compounds which is based on the rapid combustion process. The sample is burned in a fast stream of carbon dioxide–oxygen mixture in a tube provided with an empty combustion chamber. The products formed are led over hot copper, thus removing excess of oxygen and reducing the nitrogen oxides. The nitrogen is swept out with the transport gas into a nitrometer, collected over potash solution and measured. A single determination may be completed in about 20 minutes, which includes the cooling period of the nitrogen prior to measuring the volume. Compounds which burn only with difficulty when subjected to the *Pregl-Dumas* procedure have been analysed satisfactorily by the new method.

It is shown that commercial oxygen contains up to 0.07% of inert gases and is therefore unsuitable in the nitrogen method for oxidising nitrogenous chars. An electrolytic cell which provides a continuous supply of blank-free oxygen, and hydrogen for regeneration of the copper filling has been constructed as a permanent part of the apparatus.

Complete reduction of the nitrogen oxides and oxygen by the large amount of metallic copper (ca. 20 cm) is accomplished at the flow rate range of 15–20 ml per minute employed.

Evidence has been obtained that present-day quartz tubing of British manufacture becomes porous in the course of time when heated in contact with copper oxide on copper in an inert atmosphere of carbon dioxide, giving high blanks.

## Zusammenfassung.

Ein Schnellverfahren zur Mikrobestimmung von Stickstoff in organischen Verbindungen wird beschrieben. Die Probe wird in einem raschen Kohlendioxyd-Sauerstoff-Strom in einem Rohr mit besonderem T-förmigem Verbrennungsteil vergast. Die Verbrennungsprodukte leitet man über erhitztes Kupfer, um überschüssigen Sauerstoff zu entfernen und die Oxyde des Stickstoffes zu reduzieren. Der Stickstoff wird mit Hilfe des Transportgases in ein Azotometer ausgespült, über Kalilauge aufgefangen und gemessen. Eine Einzelbestimmung dauert etwa 20 Minuten einschließlich der für die Abkühlung des Azotometers nötigen Zeit. Substanzen, die nach *Pregl-Dumas* nur schwer analysierbar sind, konnten nach der neuen Methode befriedigend untersucht werden.

Handelsüblicher Sauerstoff enthält bis zu 0,07% inerte Gase und eignet sich daher nicht zur Verbrennung stickstoffhaltiger Verkohlungsprodukte.

Ein Gerät zur kontinuierlichen elektrolytischen Gewinnung blindwertfreien Sauerstoffes, das außerdem auch Wasserstoff zur Reduktion der Kupferdrahtfüllung liefert, bildet einen Teil der angegebenen Apparatur.

Die vollständige Reduktion der Stickstoffoxyde und des Sauerstoffes ist bei der Strömungsgeschwindigkeit von 15 bis 20 ml/Minute durch die große Menge metallischen Kupfers sichergestellt.

Es hat sich gezeigt, daß derzeit Quarzrohre britischer Herkunft im Lauf der Zeit beim Erhitzen in Kohlendioxydatmosphäre in Gegenwart von Kupfer oder Kupferoxyd porös werden und daher hohe Blindwerte verursachen.

**Résumé.**

On décrit une méthode pour le microdosage de l'azote dans des composés organiques, basée sur le procédé de combustion instantanée. L'échantillon est brûlé dans un rapide courant de mélange $CO_2$—$O_2$ dans un tube muni d'une chambre à combustion vide. Les produits formés sont dirigés sur du cuivre chauffé ce qui fixe l'oxygène en excès et réduit les oxydes d'azote. L'azote est balayé vers le nitromètre, recueilli sur la solution de potasse et mesuré. Une seule détermination peut se faire en 20 minutes environ y compris la période de refroidissement de l'azote avant mesure du volume. Les composés ne brûlant qu'avec difficulté quand on les traite par la méthode de *Dumas-Pregl* ont été analysés d'une manière satisfaisante quand on les traite par le nouveau procédé.

On montre que l'oxygène commercial contient jusqu'à 0,07% de gaz inertes et que par conséquent, il ne convient pas dans la méthode à l'azote pour oxyder les goudrons azotés. Une cuve à électrolyse qui fournit un débit continu d'oxygène exempt d'impuretés et de l'hydrogène pour la régénération de la tournure de cuivre a été installée comme faisant partie intégrante de l'appareil.

La réduction complète des oxydes de l'azote et de l'oxygène par le grand excès de cuivre métallique (environ 20 cm) s'effectue à la vitesse de 15 à 20 ml par minute de fonctionnement. On a mis en évidence le fait que les tubes de quartz actuellement fabriqués par les usines anglaises deviennent poreux au cours du temps quand on les chauffe dans une atmosphère inerte de gaz carbonique, ce qui donne lieu à des témoins élevés.

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## Mitteilungen aus chemischen Gesellschaften.

### Symposium on Analytical Chemistry 1954

organised by the

**Midland Society for Analytical Chemistry Great Britain.**

Arising from the success of the short Symposium on Analytical Chemistry held in Birmingham in 1952, it is proposed to run a larger Symposium from August 25th to September 1st, 1954. This will consist of original papers and recent advances in various analytical fields.

An exhibition of new and special apparatus will be held simultaneously and visits to local places of interest will be organised.

A Ladies' Committee has been formed to organise entertainment for non-scientific visitors.

Further details will be made available at a later date.

*J. W. Robinson*, B. Sc., Ph. D., A. R. I. C.,
(Symposium Secretary),
Post Office Engineering Department,
Birmingham, 9, England.

## Society of Public Analysts and Other Analytical Chemists.

### Ordinary Meeting of the Society.

An Ordinary Meeting of the Society (organised jointly by the Microchemistry Group and the Scottish Section) was held at 7.15 p. m. on Wednesday, May 6th, 1953, in the Chemistry Department, University of Glasgow. The Chair was taken by the President, Dr. *D. W. Kent-Jones*, F. R. I. C., and the following papers were presented and discussed:

"Geochemistry and Microchemistry", by *David T. Gibson*, D. Sc.

Many of the most valuable scientific advances have been made either by extending ordinary investigations to extreme lengths or by exploiting the borderlands between two so-called distinct sciences.

Geochemistry may be regarded as a combination of both these, for it extends the study of chemistry in space and time and temperature and it takes evidence from astronomy, biology and geology. It is of particular

interest that it has been by the microchemical determination of the rarer components of ordinary rocks that *Goldschmidt* was able to rationalise the cycles of elements in space and time. Nearly all his work was done by quantitative emission spectroscopy and while it was rigorously controlled by comparison with synthetic specimens, it was of necessity limited in scope and by shortage of collaborators. A much more comprehensive survey of the possibilities of *Goldschmidt*'s methods is being envisaged in the U. S. As a preliminary, a large amount of carefully mixed natural rock standards are being accumulated. These will ultimately serve as a more dependable control for spectroscopic methods, but from the interim report ("A Co-operative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analyses of Silicate Rocks", U. S. Geological Survey Bulletin No. 980, 1951) it is evident that much work on classical lines remains to be done before an adequate consensus of analytical opinion can be reached.

"Microanalysis of Silicate Rocks. Part IV. The Determination of Alumina", by *Christina C. Miller*, Ph. D., D. Sc., F. R. S. E., F. H.-W. C., and *Robert A. Chalmers*, B. Sc.

The complications attending the classical method of determination of alumina in silicate rocks, and difficulties peculiar to the micro-scale, were reviewed. Earlier attempts by microchemists to devise an improved method for the determination of alumina were briefly described.

A new procedure was presented for the separation and direct determination of alumina in 5-mg samples of silicate rocks. Silica is eliminated by means of hydrofluoric and sulphuric acids, and the residue is fused with potassium bisulphate and extracted with acid. Several metals together are eliminated with cupferron and an organic solvent, and then aluminium is extracted as the acetylacetone complex, and finally converted into aluminium 8-hydroxyquinolinate.

"Microchemical Determination of Sulphur in Organic Compounds", by *Williams H. Massie*, B. Sc., Ph. D., A. R. I. C.

Organic compounds that contain nitrogen in addition to sulphur give, on combustion in oxygen over platinum, a non quantitative yield of nitrous and nitric acids whose presence render worthless the simple and rapid microtitrimetric procedure for sulphur as sulphuric acid.

A number of modified volumetric methods for the estimation of sulphur in this type of compound have been described, but none is completely satisfactory owing to involved technique or to defects inherent in the method.

A promising physico-chemical titrimetric method, supported by analytical results, was advanced as a suggestion for the direction of future work on this subject.

The Meeting was preceded by an afternoon visit to the Clydebridge Steel Works of Colvilles Ltd.

## Ordinary Meeting of the Society.

An Ordinary Meeting of the Society was held at 7 p. m. on Wednesday, May 20th, 1953, in the Meeting Room of the Chemical Society, Burlington House, London W. 1. The President, Dr. *D. W. Kent-Jones*, F. R. I. C., was in the Chair, and the following papers were presented and discussed:

"The Determination of Ergosterol in Yeast", by *W. H. C. Shaw*, Ph. C., F. R. I. C., and *J. P. Jefferies*, B. Sc., A. R. I. C.

"Part I. The Ultra-violet Absorption of Purified Ergosterol".

Most published records agree on the wavelengths of the three main peaks in the ultra-violet absorption curve of ergosterol, but there are discrepancies in the extinction values reported for the various maxima, apparently because of the difficulty of preparing pure ergosterol by direct recrystallisation of the commercial material and to a lesser extent because of small variations in the moisture content of the hydrated sterol. Simple recrystallisation does not always yield a pure product; the best means of purification is by recrystallising a suitable ester, with subsequent regeneration of the sterol.

The preparation and purification of ergosterol benzoate was described and the physical properties and ultra-violet absorption (in various solvents) of a purified specimen of ergosterol were recorded.

"Part II. Determination by Saponification and Ultra-violet Absorption Spectroscopy".

Part of the ergosterol found in yeast occurs in a combined form, and treatment to liberate the free sterol is a necessary preliminary to its determination. Most published methods make use of alcoholic or aqueous alkali hydroxides for this purpose, and the variety of strengths prescribed suggested that further investigation was necessary.

The conditions for the destruction of the yeast cells and maximum recovery of ergosterol have been studied. It was found that boiling under reflux with alcoholic sodium or potassium hydroxides did not break down the yeast sufficiently. Aqueous sodium hydroxide at strengths from 10 to 50 per cent. w/w gave low and erratic results, additional ergosterol being recovered by subsequent alcoholic saponification of the residue.

Concentrations of potassium hydroxide above 20 per cent. w/w in aqueous solution proved satisfactory, the strength required depending on the length of boiling under reflux. For the method described 40 per cent. w/w aqueous potassium hydroxide has been selected, as it makes possible considerable latitude in time and concentration.

The ergosterol in the extracted unsaponifiable matter is separated by digitonin precipitation from non-sterol substances that show irrelevant absorption in the same region as ergosterol. This precipitation has been shown to be quantitative, the separated sterol digitonides yielding solutions spectroscopically indistinguishable at wavelengths above 260 mμ from those of purified ergosterol.

"Part III. Corrections for Irrelevant Absorption in Solutions of Ergosterol".

The unsaponifiable matter of yeast normally contains substances that possess ultra-violet absorption in the same region as ergosterol, so that the extinction at the ergosterol maximum (282 mμ in absolute alcohol) cannot be used directly as a measure of the concentration of ergosterol present. Although the digitonin purification described in Part II may be used for separating ergosterol in a spectroscopically pure condition, considerable time can be saved by applying a correction procedure to the gross absorption.

Two such procedures have been studied: (i) a correction of the *Morton* and *Stubbs* type, based on the 282-mμ maximum and two subsidiary wavelengths at which the purified compound possesses 6/7 maximum absorption,

and (ii) a new four-point correction based on the three ergosterol maxima (271.5, 282, and 293.5 m$\mu$) with a fourth reading at 310 m$\mu$, where ergosterol shows very little absorption.

Procedure (i) suffers from the disadvantage that the maxima in the absorption curve of ergosterol are sharp and observations at the subsidiary wavelengths must be taken on steep portions of the curve. In consequence small errors in measuring wavelengths have a large effect on the correction factor and any instrument used for this procedure must be calibrated with pure ergosterol. Procedure (ii) is free from this disadvantage but requires a greater range of wavelengths and linearity of absorption must be assumed over it.

Results by both corrective procedures were compared with those by the full digitonin method previously described. The degree of agreement is generally good, but depends on the shape and amount of irrelevant absorption which has been determined on a number of different strains of yeasts.

"Part IV. A Short Method Based on Ultra-violet Absorption".

An accurate method for determining ergosterol in yeast has been described in Part II; it involves saponification, extraction of unsaponifiable matter, digitonin precipitation and subsequent spectroscopic determination and has proved too lengthy for the examination of large numbers of samples.

For this purpose, a short semi-micro method was described: it involves saponifying a portion of the yeast sample containing about 1 mg of ergosterol with a small volume of 40 per cent. w/w aqueous potassium hydroxide in a specially designed flask and extracting the unsaponifiable matter with a single accurately measured volume of cyclohexane. The filtered extract is suitable for spectroscopic examination. The four-point correction procedure described in Part III is applied to allow for irrelevant absorption; the ergosterol content of the sample is calculated from the corrected extinction at 282 m$\mu$ (max.).

The method requires much less manipulation time than the full digitonin procedure but, because a geometrical correction and a single extraction only are used, gives results slightly lower and a standard deviation of a single determination a little greater than are got with the full method.

"The Estimation of Micro Quantities of Calcium", by *G. E. Harrison*, Ph. D., F. Inst. P., and *W. H. A. Raymond*.

A micro method for the estimation of calcium was described; it is based on the colorimetric estimation of a molybdenum thiocyanate. An accuracy of better than 10 per cent. is attained for solutions containing as little as 4 $\mu$g of calcium.

The method is especially useful for the estimation of serum calcium in young children or small laboratory animals.

A comparison of the results with those found by other methods was given.

"The Ultra-violet Spectrophotometric Estimation of the Quality of Mineral Oils Extracted from Bread", by *M. A. Cookson*, B. Sc., A. R. I. C., *J. B. M. Coppock*, B. Sc., Ph. D., F. R. I. C., and *R. Schnurmann*, M. Sc., Dr. Rer. Nat.

oil A method has been developed by which the degree of refining of a mineral that has been absorbed by a dough during bread making may be determined

in the resultant bread. The method consists basically of sulphating, under controlled conditions, the unsaponifiable fraction of the total oils extracted from bread, so that the natural saponifiable matter is destroyed without completely removing the unsaturated hydrocarbon constituents inherent in mineral oils of different degrees of refining. The recovered mineral oil is then examined by ultra-violet absorption spectrophotometry to determine its quality. A spectrophotometric criterion was suggested for the quality of mineral oils that could be regarded as satisfactory for the lubrication of plant used in bread production.

## Joint Meeting of the Physical Methods Group.

The Forty-first Ordinary Meeting of the Physical Methods Group of the Society was held at 6.00 p. m. on Friday, May 8th, 1953, in the Oriental Cafe, Ipswich. This was a joint meeting with the East Anglian Section of the Royal Institute of Chemistry. Dr. *J. Haslam* was in the Chair and about 38 members and visitors were present.

The following papers on "Emission spectroscopy" were presented and discussed.

"Semiquantitative Techniques in Spectrochemical Analysis", by *R. L. Mitchell*, B. Sc., Ph. D., F. R. I. C.

There is often a need for something between a purely qualitative examination of a sample and an exact, time consuming, quantitative determination of one or more constituents. Several spectrochemical procedures which can provide the necessary information have been described. In this respect spectroscopic methods are generally somewhat more flexible than other analytical procedures. The semiquantitative approach is particularly valuable for the survey of a number of constituents in a large number of samples.

The approach to the problem has varied with different workers, and several of the methods suggested were reviewed. That in use at The Macaulay Institute for Soil Research for estimations of this type, particularly in soils, rocks and minerals, involves cathode layer excitation, followed by visual comparison of the spectrograms with those of standard samples of like matrix composition in a spectral line comparator.

"Some Techniques of Presentation of Sample to the Spectrograph", by *A. H. C. P. Gillieson*, B. Sc., Ph. D.

Four methods of sample presentation were described — three arc and one spark. They are all essentially methods for detection and estimation of trace elements; two are quantitative, the others semiquantitative.

1. Copper-Arc using Flux plus sample.
2. Carrier-Distillation D. C. Graphite Arc.
3. Hollow Cathode Discharge Tube.
4. Copper Spark plus Sample Solution.

The first is a quantitative method of wide application suitable for a wide variety of element oxides or other compounds, e. g. plant ashes, ignited soils, and ores.

The second is suitable for the determination of impurities in refractories, e. g. alumina, beryllia, etc.

The third, for which either solid samples or solutions may be used, is particularly useful for the determination of the halides, but will also determine the alkali metals and sulphur. It can be applied direct to organic materials.

The last—a solution method—is of wide application where the amount of material available is very small in quantity.

"Applications of the Porous Cup Technique", by *L. G. Young.*

A modification of the porous cup technique of *Feldman* has been applied to the determination of a major constituent—zinc in brass. Details include the preparation of electrodes, analytical procedure and a new electrode stand designed for this work. Tables showing the reproducibility and accuracy of single determinations were presented. Mention is made of other metallurgical samples analysed and of various difficulties already overcome in the application of the method to the complete analysis of soluble miscellaneous residues, ashes and corrosion products.

The meeting was preceded by a visit to the Research Laboratories of B. X. Plastics, Manningtree.

## Buchbesprechungen.

*Clément Duval:* **Inorganic Thermogravimetric Analysis.** With an Introduction by *Pierre Chevenard.* Mit 152 Textabb. XV, 531 S. Amsterdam: Elsevier Publishing Co. 1953. £ 3/-/-.

Schon vor Jahren hat *Feigl* die thermogravimetrischen Arbeiten *Duvals* als die „Pathologische Anatomie der Analytischen Chemie" bezeichnet und hat damit der Bedeutung thermogravimetrischer „Sektionsbefunde" ähnliche Wichtigkeit für den Analytiker zuerkannt, wie sie der Kliniker den Untersuchungen des Pathologen einräumt. In gewisser Hinsicht mag sogar der objektive Befund der automatisch registrierenden Thermowaage der Autopsie überlegen sein. Die zahlreichen Publikationen *Duvals* und seiner Schule, die über die Untersuchungen von rund 1000 verschiedenen Fällungsmethoden berichten, haben daher auch hervorragendes Interesse in der Fachwelt gefunden.

Das vorliegende Buch bietet eine imponierende Schau über die Leistungen auf diesem Gebiet. Sein erster Teil bringt die Beschreibung der Thermowaage von *Chevenard,* ihrer Ausgestaltung zu einem vollautomatischen Gerät und ihrer methodischen Anwendung. Der zweite Teil umfaßt in zahlreichen Einzeldarstellungen die Ergebnisse der Untersuchungen verschiedenster Niederschläge von zusammen 62 Elementen. Die Eignung oder Nichteignung dieser Substanzen für die gravimetrische Bestimmung und die bei diesen Bestimmungen einzuhaltenden Arbeitsbedingungen lassen sich aus diesen Ergebnissen klar erkennen. Hiermit ist ein Erfahrungsschatz gewonnen, den jeder Analytiker als wertvollstes Geschenk dankbar empfangen wird. Daß der Verfasser darüber hinaus auch noch eine Reihe sonstiger Anwendungsmöglichkeiten der Thermowaage beschreibt — z. B. für die Reinheitsprüfung — sei nur nebenbei erwähnt.

Es besteht kein Zweifel, daß dieses Buch der quantitativen anorganischen Analytik höchst bedeutungsvolle Anregungen und Hilfen bietet, deren ungenügende Beachtung ein schwerer Fehler wäre. *M. K. Zacherl*-Wien.

*Theodor Leipert, Walter Piringer* und *Walter Pilgerstorfer:* **Laboratoriumsdiagnostik.** Mit 15 teils farbigen Tafeln und 124 Textabb. XII, 736 S. Wien: Urban u. Schwarzenberg. 1953. Ganzln. S 450.—.

Aus der Zusammenarbeit von Chemiker, Bakteriologen und Kliniker entstanden, liegt ein Buch vor, das sich in vorteilhaftester Weise von so vielfach üblichen Methodenbüchern des klinischen Laboratoriums unterscheidet. Es ist nicht nur geeignet, für alle modernen Untersuchungsverfahren des medizinischen Laboratoriums gute und ins Detail gehende Arbeitsvorschriften zu bieten und die Ergebnisse dieser Untersuchungen diagnostisch zu deuten, sondern es zeigt vor allem auch dem behandelnden Arzt und

Kliniker, in wie vielfacher Hinsicht sich das Laboratorium zu einer unentbehrlichen Hilfe bei der kunstgerechten Untersuchung und Behandlung seiner Patienten entwickelt hat, wobei auf die enge Zusammenarbeit zwischen Arzt und Laboratorium selbstverständlich der größte Wert gelegt wird.

Die vielen Methoden zur Untersuchung von Körperflüssigkeiten, Stoffwechselprodukten und Organfunktionen sind nicht nur nach dem jeweiligen Untersuchungsmaterial, sondern auch nach den hierfür in Betracht kommenden Hilfsmitteln mikroskopischer, physikalischer oder chemischer Art übersichtlich angeordnet und daher leicht auffindbar. Den Beschreibungen jedes einzelnen Verfahrens, die hinsichtlich ihrer praktischen Verwertbarkeit keinen Wunsch offenlassen, folgen in kurzen, aber klaren Absätzen Anweisungen zur Beurteilung des Untersuchungsergebnisses, aus denen das auf reicher Erfahrung begründete kritische Verantwortungsbewußtsein der Verfasser zu entnehmen ist. Damit wird der Gefahr begegnet, dem Laboratorium mehr zuzumuten, als es zu leisten vermag.

Das seitens des Verlages gut ausgestattete Buch wird insbesondere auch wegen seiner vielen Abbildungen, die eine wertvolle Ergänzung des Textes darstellen, Anklang finden. Es ist ihm weite Verbreitung zu wünschen.

*M. K. Zacherl*-Wien.

*Th. Lieser:* **Kurzes Lehrbuch der Cellulosechemie.** Mit 88 Abb. und 4 photographischen Tafeln. V, 288 S. Berlin-Nikolassee: Gebrüder Borntraeger. 1953. Geb. DM 36,—.

Mit großem Geschick ist auf engem Raum das große Gebiet der Cellulosechemie in seinen wesentlichen Teilen abgehandelt, unterstützt durch eine Reihe guter Abbildungen und schematischer Darstellungen. Dem Wesen eines Lehrbuches entsprechend wird die Entwicklung der neueren Erkenntnisse über Cellulose im allgemeinen und einige wichtige Cellulosederivate im besonderen dargestellt, wobei die theoretischen Grundlagen aufgezeigt und darüber hinaus auch wertvolle Hinweise für die angewandte Cellulosechemie gegeben werden. Auch bei der Darstellung gegensätzlicher theoretischer Anschauungen (makromolekulare oder micellare Natur der Cellulose) sucht der Verfasser das Allgemeingültige und für die weitere Entwicklung Wesentliche der verschiedenen Theorien herauszuheben. Trotz der Fülle des gebotenen Stoffes wäre empfehlenswert, bei einer künftigen Neuauflage des Buches Ergänzungen auf einigen wichtigen Teilgebieten (Polydispersität, Strukturviskosität, Deformationsvorgänge in Regeneratcellulosen, Lichtabbau u. a.) vorzusehen und die bezügliche neuere Literatur, insbesondere auch die des Auslandes zu zitieren. Auch die reiche neuere Literatur über die verschiedenen Hemicellulosen wäre eingehender zu berücksichtigen. Wenn der Referent solche Wünsche zum Ausdruck bringt, so soll dies der allgemeinen Feststellung keinen Abbruch tun, daß das Werk als solches wohl gelungen ist und einem im deutschen Sprachraum schon seit langem fühlbaren Bedürfnis entgegenkommt, wofür dem verdienstvollen Verfasser insbesondere auch von den studierenden Fachgenossen aufrichtiger Dank gebührt.

*Th. Kleinert*-Lenzing.

*Hans Vogel:* **Chemie und Technik der Vitamine.** 3. Aufl. Bearbeitet von Doz. Dr. *H. Knobloch.* Zwei Bände. II. Band: Die wasserlöslichen Vitamine. 1. Lieferung, 160 S. Stuttgart: F. Enke. 1953. Geh. DM 26,—.

Zwischen dem Erscheinen des ersten Bandes über die fettlöslichen Vitamine im Jahre 1950 und der Herausgabe der ersten Lieferung des zweiten Bandes

ist ein längerer Zeitraum verstrichen, als vorgesehen war. Gerade auf dem Gebiete der wasserlöslichen Vitamine sind ja in den letzten Jahren besonders viele neue Entdeckungen gemacht worden, die zu verarbeiten waren. Um das Erscheinen des zweiten Bandes nicht noch weiter hinauszuzögern, hat sich der Verlag entschlossen, diesen in Form von sechs Einzellieferungen herauszubringen, die in Abständen von etwa zwei Monaten einander folgen sollen. Die Behandlung der wasserlöslichen Vitamine soll in folgender Reihenfolge vorgenommen werden: Vitamin $B_1$, $B_2$, $B_{12}$, Pteroylglutaminsäure, Biotin, Nikotinsäureamid, die anderen Vitamine der B-Gruppe, Vitamin C, P.

Die erste Lieferung umfaßt das Vitamin $B_1$ (128 S.) und den ersten Teil über das Vitamin $B_2$ (32 S.). Die Art der Anordnung entspricht in stofflicher Hinsicht der des ersten Bandes: Geschichte, Vorkommen, Konstitution, Synthese, Eigenschaften, Abbau, Derivate, Nachweis und Bestimmung, Einheiten, Bedarf, Pharmakologie, Biosynthese, Wirkungsweise, Technologie mit Patentverzeichnis und ein umfassendes Verzeichnis der Literatur, die bis etwa Mitte 1952 berücksichtigt ist. Soweit wir aus der ersten Lieferung ersehen, wird sich auch der zweite Band dem ersten würdig anschließen und für jeden an Vitaminen Interessierten unentbehrlich sein.

*F. Wessely*-Wien.

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